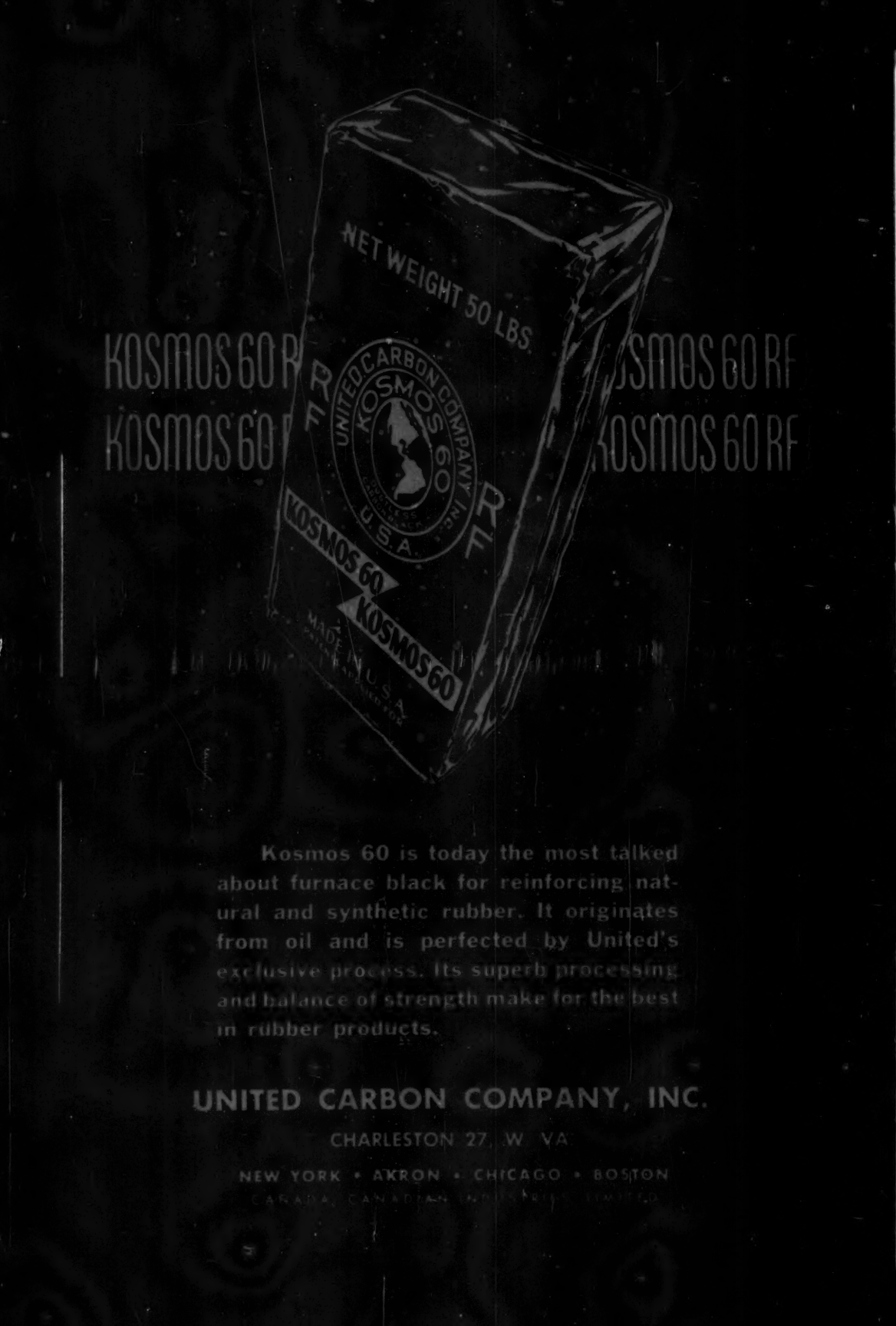
RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XXIII NUMBER 4

October-December, 1950

Published Quarterly under the Auspices of the
DIVISION OF RUBBER CHEMISTRY
of the
AMERICAN CHEMICAL SOCIETY
at Prince and Lemon Sts., Lancaster, Pa.



Kosmos 60 is today the most talked about furnace black for reinforcing natural and synthetic rubber. It originates from oil and is perfected by United's exclusive process. Its superb processing and balance of strength make for the best in rubber products.

UNITED CARBON COMPANY, INC.

CHARLESTON 27, W VA

NEW YORK • AKRON • CHICAGO • BOSTON

CANADA: CANADIAN [illegible] LIMITED

See what **Philblack*** *can do for YOUR RUBBER PRODUCTS*

PHILBLACK A

The MAF black for better tire carcass and mechanical goods stocks . . . low heat buildup and excellent processing characteristics.

PHILBLACK O

The HAF black for tire treads . . . exceptionally high abrasion resistance and long flex life . . . particularly with "cold" rubber.

PHILLIPS CHEMICAL COMPANY

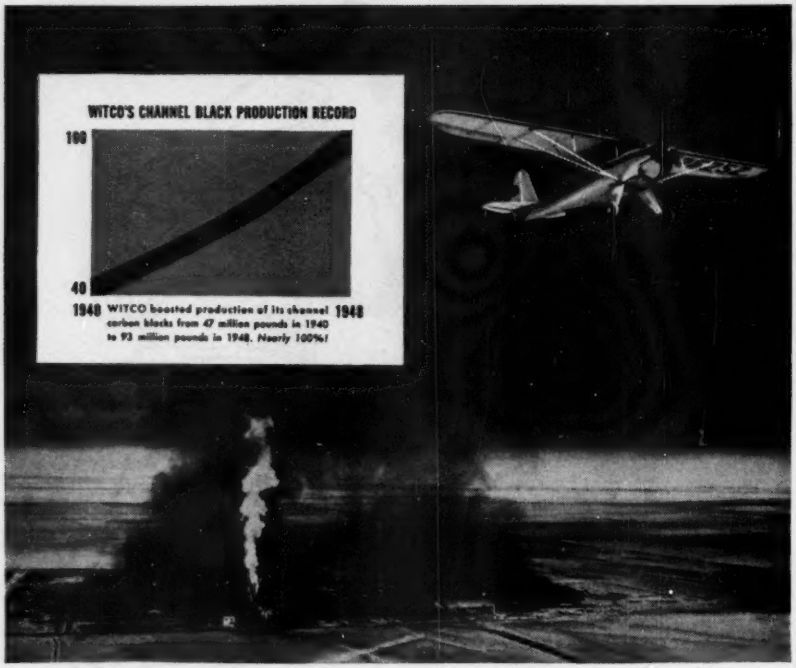
PHILBLACK SALES DIVISION

EVANS BUILDING · AKRON 8, OHIO

Warehouses in Akron, Boston, Chicago, and Trenton
West Coast agent: Harwick Standard Chemical Company, Los Angeles
Canadian agent: H. L. Blachford, Ltd., Montreal and Toronto

*A Trademark

Entered as second-class matter March 19, 1943, at the Post Office at Lancaster, Pa., under the Act of August 24, 1912. Acceptance for mailing at special rate of postage provided for in paragraph (d-2). Section 34.40, P. L. and R. of 1948, authorized September 25, 1940.


WITCO'S CHANNEL BLACK PRODUCTION RECORD
100
40
1940
1948
WITCO boosted production of its channel carbon blacks from 47 million pounds in 1940 to 93 million pounds in 1948. Nearly 100%!

The burners in **WITCO'S** channel black installations are burning up **production records,** too

As the graph shows, more and more tiny flames, burning day and night, have increased Witco's production of Continental Channel Blacks during 1940 through 1948 from *47 million pounds to 93 million pounds!*

In Continental Channel Blacks, Witco offers a complete, highly specialized line of products for specific needs in all types of rubber compounding—constantly controlled and improved by laboratory and pilot plant research.

Write for samples of WITCO and CONTINENTAL Carbon Blacks for your own staff to evaluate. Or send for complete information.

WITCO CHEMICAL COMPANY
CONTINENTAL CARBON COMPANY
295 Madison Avenue, New York 17, N. Y.

Boston • Chicago • Detroit • Cleveland • Los Angeles • San Francisco • Akron • Amarillo • London and Manchester, England

DOUBLE-CHECKED ✓ CHEMICALS FOR THE RUBBER INDUSTRY

THE "9" SERIES XTRUDED SHARPLES ACCELERATORS

For those who prefer extruded products, Sharples offers a line of ultra accelerators in this form. Other grades in powder form are also available from our plant and warehouses.

SA 52-9 TetraMETHYLthiuram DIsulfide
SA 57-9 ZINC diMETHYLdithiocarbamate
SA 62-9 TetraETHYLthiuram DIsulfide
SA 66-9 SELENIUM diETHYLdithiocarbamate
SA 67-9 ZINC diETHYLdithiocarbamate
SA 77-9 ZINC diBUTYLdithiocarbamate

For samples, prices and other information write Dept. R

SHARPLES CHEMICALS INC.

SHARPLES TRADE ✓ MARK CHEMICALS

SALES OFFICES:
350 FIFTH AVENUE, NEW YORK
34 CHERRY STREET, AKRON
80 E. JACKSON BLVD., CHICAGO

Thiokol*

SYNTHETIC RUBBERS and RUBBER CHEMICALS

CRUDES:

TYPE A — for stocks requiring unsurpassed solvent resistance.

TYPE FA — for extruded goods that must withstand aromatic blended fuels and permanent oil and weather-resistant putties.

TYPE PR-1 — for molded goods that must withstand aromatic blended fuels.

TYPE ST — for molded and extruded goods that must withstand aromatic blended fuels and low temperatures.

WATER DISPERSIONS:

MX & WD-6 — for liquid compounds to give films of high solvent and moisture resistance.

MF — for liquid compounds to give films of good solvent and low temperature resistance.

WD-2 — For liquid compounds to give films which must be free from odor. Films also have excellent low temperature resistance.

PLASTICIZERS:

TP-90B — for plasticizing natural rubber, GR-S, Buna N and GR-M for extreme low temperature resistance.

TP-95 — for plasticizing Buna N rubbers, GR-M and vinyl resins for excellent low temperature resistance and good heat resistance.

LIQUID POLYMERS:

LP-2 — A liquid polymer of 100% solids which vulcanizes to a tough resilient solid without shrinkage when mixed with curing agents.

LP-3 — same as LP-2 but of a lower viscosity.

TACKIFIERS:

GALEX W-100 & W-100D — A non-oxidizing rosin for imparting tack to the Buna rubbers. Also valuable in GR-M compounds.

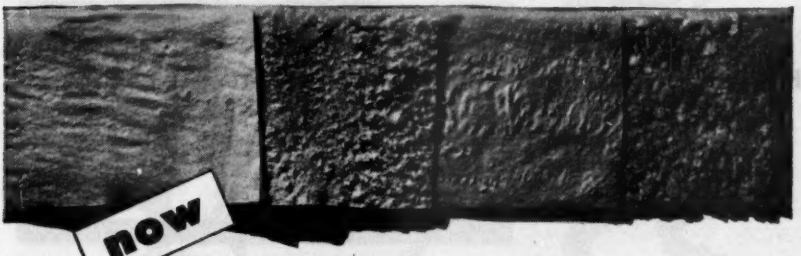
TECHNICAL INFORMATION AND SAMPLES ON REQUEST

Thiokol CORPORATION
781 NORTH CLINTON AVENUE
TRENTON • NEW JERSEY

*THIOKOL, REG. U.S. PAT. OFF.

Superior dispersion characteristics of **Pliolite S-6B**, compared with three competitive resins. All samples were processed under identical techniques so established as to give "marginal mixing conditions." Such conditions approximate the absolute minimum required in production equipment for acceptable dispersion of any reinforcing resin. See for yourself, the exceptional dispersion characteristics of **Pliolite S-6B** as evidenced by the smooth-textured sheet and the minimum of undispersed resin particles.

Pliolite S-6B *Competitor A* *Competitor B* *Competitor C*



now for shoe soles

a reinforcing resin that's *truly* easy to process

USE PROVED *Products*

PLIOLITE S-6B

YOU'VE probably heard about the interesting paper, delivered by Goodyear's rubber chemists before the April meeting of the Division of Rubber Chemistry of the American Chemical Society, concerning "easy processing" reinforcing resins. Well, here's the resin that resulted from their study—**Pliolite S-6B**—a truly easy processing resin. **Pliolite S-6B** has been thoroughly tested in laboratory and trial plant runs—already has been "use-proved" in full scale production by independent sole manufacturers.

Just look at the actual test samples pictured above. Note the poor dispersion indicated by rough irregular sheets and presence of undispersed resin particles in samples "A," "B" and "C." Then compare with the **Pliolite S-6B** sample showing smooth texture and readily apparent, complete dispersion and compatibility—*definite proof that* **Pliolite S-6B** *leads in easy processibility.*

In addition to easier processing, **Pliolite S-6B** will give you lighter color, high hardness and greater flex-life than most competitive resins in shoe sole stocks. What's more you can replace the present resin in your formulations, part for part, with **Pliolite S-6B** with perfect confidence and gratifying results. There's no need for lengthy evaluations of this new resin.

Ask us today for full details and samples of **Pliolite S-6B** the new, easier processing reinforcing resin for your shoe soles, wire insulation, flooring or molded items. Write to:

GOODYEAR, CHEMICAL DIVISION
AKRON 16, OHIO

GOODYEAR

Pliolite—T. M. The Goodyear Tire & Rubber Company, Akron, Ohio

product improvers for rubber compounders

HYCAR NITRILE RUBBERS—have excellent processing characteristics and proven uniformity. Exceptional resistance to heat, abrasion, cold flow and solvents.

HYCAR POLYACRYLIC RUBBERS—have superb heat resistance, and unusually high resistance to deformation at high temperatures. Excellent flexing and ozone resistance.

GOOD-RITE RESIN 50—(Reg. U.S. Pat. Off.) a low gravity reinforcing resin, first in a series of new resins for rubber compounding. Easy processing—and a highly valuable processing aid for hard compounds. Excellent compatibility with natural and synthetic rubbers.

Hycar
Reg. U.S. Pat. Off.
American Rubber

For information, please write Dept. HB-4

B. F. Goodrich Chemical Company
A DIVISION OF THE B. F. GOODRICH COMPANY
ROSE BUILDING CLEVELAND 15, OHIO

...shod for the job

In shoeing a horse, the blacksmith selects shoes best fitted in weight and balance for the job the horse is to do.

When you consider the job to be done, and select **TEXAS "E"** or **TEXAS "M"** Channel Black, you are assured highest, uniform quality and maximum economy-in-use.

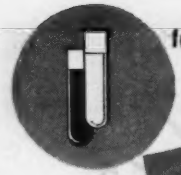
The Sid Richardson Carbon Company, owning and operating the world's largest channel black plant, has the production facilities and natural resources to meet all your present and future requirements.

Let us help you get the job done.

TEXAS CHANNEL BLACKS

Sid Richardson
CARBON CO.
FORT WORTH, TEXAS

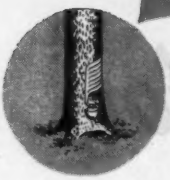
GENERAL SALES OFFICES
EVANS SAVINGS AND LOAN BUILDING
AKRON 8, OHIO



for Synthetic Rubber

SANTOCURE

cuts costs and improves quality



for Natural Rubber

for Reclaimed Rubber

Since prewar days, Monsanto Santocure has been the superior accelerator for vulcanizing rubber. It is a dependable, hard-working accelerator for natural, synthetic or reclaimed rubber, cutting acceleration costs, improving quality and adding a greater margin of processing safety. Santocure requires no special technique or handling. Santocure is available for immediate shipment. Mail the coupon for information. MONSANTO CHEMICAL COMPANY, Rubber Service Department, 920 Brown St., Akron 11, Ohio.

MONSANTO CHEMICALS FOR THE RUBBER INDUSTRY

ANTIOXIDANTS

Flectol H*
Santoflex* B
Santoflex BX
Santoflex 35
Santowhite* Crystals
Santowhite MK

ALDEHYDE AMINE ACCELERATORS

A-32
A-77*
A-100

MERCAPTO ACCELERATORS

Santocure*
El-Sixty*
Ureka Base*
Ureka C
Mertax
Thiotax (2-Mercapto benzo thiazole)
Thiofide* (2,2' dithio-bis benzo thiazole)

GUANIDINE ACCELERATORS

Diphenylguanidine (D. P. G.)
Guantal*

ULTRA ACCELERATORS FOR LATEX, ETC.

R-2 Crystals
Pip-Pip
Thiurad*
Ethyl Thiurad (Tetra ethyl thiuram disulfide)
Mono Thiurad (Tetra methyl thiuram mono sulfide)
Methasan* (Zinc salt of dimethyl dithiocarbamic acid)
Ethasan* (Zinc salt of diethyl dithiocarbamic acid)
Butasan* (Zinc salt of dibutyl dithiocarbamic acid)

WETTING AGENTS AND DETERGENTS

Areskap* 50
Aresklene* 375
Santomerse* S
Santomerse D

MISCELLANEOUS MATERIALS

Thiocarbanilide ("A-1")
Santovar* A
Santovar O
Insoluble Sulfur "60"
Retarder ASA

COLORS REODORANTS

*Reg. U. S. Pat. Off.

MONSANTO
CHEMICALS — PLASTICS

MONSANTO CHEMICAL COMPANY
Rubber Service Department
920 Brown Street, Akron 11, Ohio

Without cost or obligation, please send information on Santocure; and on.....

.....

Name.....*Title*.....

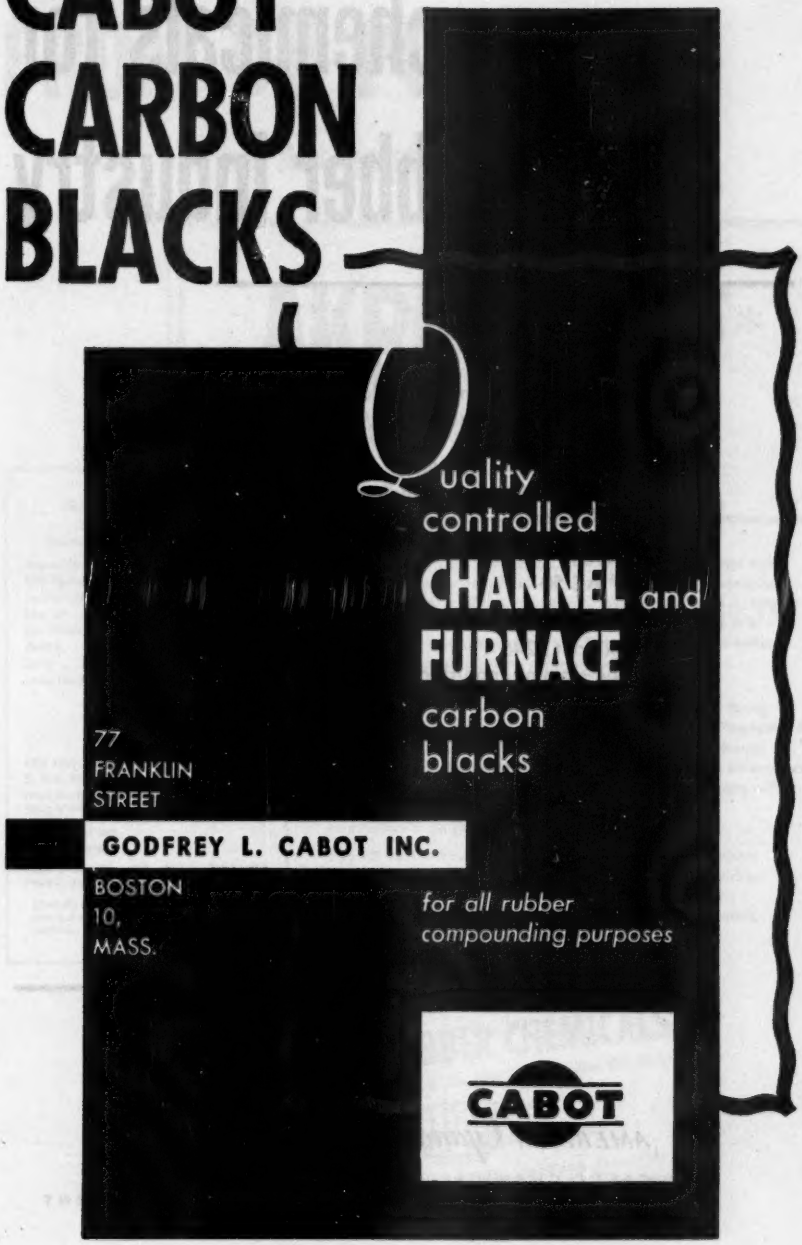
Company.....

Street.....

City.....*Zone*...*State*.....

SERVING INDUSTRY . . . WHICH SERVES MANKIND

CABOT CARBON BLACKS



chemicals for the rubber industry

ACCELERATORS
Thiazoles
MBT (Mercaptobenzothiazole)
MBTS (Benzothiazyldisulfide)
Guanidine
DPG (Diphenylguanidine)
DOTG (Diorthotolylguanidine)
Accelerator 49

ACTIVATOR
Aero* AC 50

ANTIOXIDANT
Antioxidant 2246
(Non-staining, non-discoloring type)

PEPTIZER
Pepton® 22

RETARDER
Calco Retarder P.D.

STIFFENING AGENT
Calco S.A.

SULFUR
Rubber Maker's Grade

*Trade-mark

Calco

AMERICAN Cyanamid COMPANY

CALCO CHEMICAL DIVISION
INTERMEDIATE & RUBBER CHEMICALS DEPARTMENT
BOUND BROOK, NEW JERSEY, U.S.A.

FROM DU PONT...

a new flex-resisting antioxidant

AKROFLEX F*

efficient and economical

Comparison of Akroflex F and Thermoflex A

Cure for flexing rate: 45 minutes at 287°F.

Smoked Sheets	100.0
MPC Carbon Black	50.0
Stearic Acid	3.0
Pine Tar	1.5
Zinc Oxide	5.0
ZENITE	1.25
Sulfur	3.0
Antioxidant	As Indicated

	Amount and Kind of Antioxidant			
	—0.5%—		—1.0%—	
	Akroflex F	Thermoflex A	Akroflex F	Thermoflex A
After aging 7 days in 70°C. air oven				
Hours to rating of 1†	46.7	53.9	66.8	68.7
Hours to rating of 5	77.7	89.0	123.0	122.3
After aging 14 days in 70°C. air oven				
Hours to rating of 1	29.4	30.1	40.7	43.9
Hours to rating of 5	54.1	56.1	77.6	81.4

†Each figure in this table represents the average time to a given flex rating based upon tests on 27 specimens.

Akroflex F is a unique new anti-flex cracking antioxidant fortified with a booster. It has important advantages over conventional antioxidants or mixtures of them. In efficiency it is almost equal to Thermoflex A, long the standard of excellence among all flex-resisting antioxidants. It is economical . . . costs one-third less than Thermoflex A. And its melting point is high enough to prevent caking or packing in storage. Yet it is low enough to assure excellent dispersion.

The data in the table, based on results of tests on the Du Pont flexing machine, show the effectiveness of Akroflex F compared with Thermoflex A. A rating of 1 indicates cracking has just started; a rating of 5 denotes moderately severe cracking. For all practical purposes, the two antioxidants proved equally effective. And results on 8.20 x 15 tires, road-tested with "half and half" treads, confirmed that there was essentially no difference in the performance of the two materials.

You will want to try Akroflex F at your first opportunity. Complete information will be found in our recent Report 50-2. Extra copies are available. For samples, see your Du Pont representative or write E. I. du Pont de Nemours & Co. (Inc.), Rubber Chemicals Division, Wilmington 98, Delaware.

*U. S. PAT. NO. 2,406,732

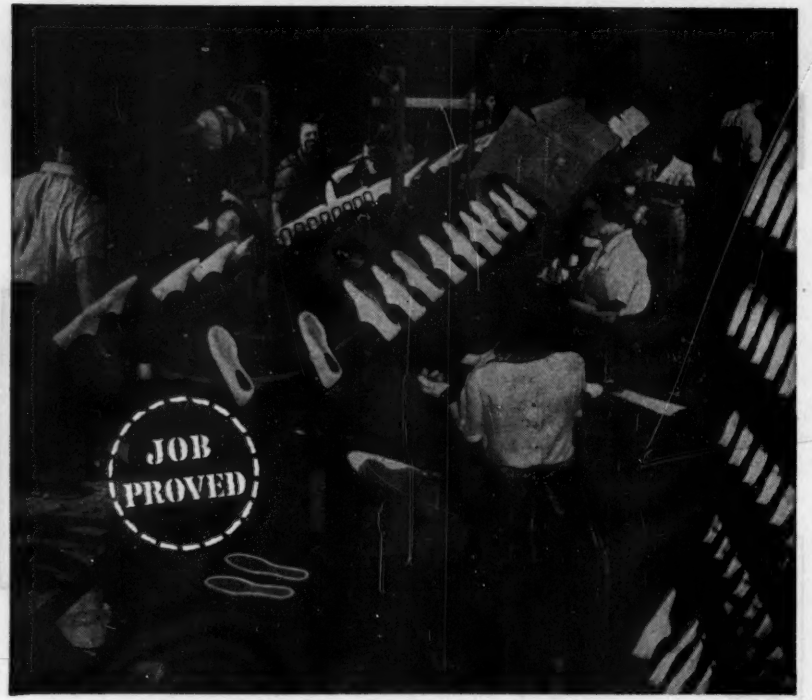
DU PONT RUBBER CHEMICALS

E. I. du Pont de Nemours & Co. (Inc.), Wilmington 98, Del.

DU PONT

REG. U.S. PAT. OFF.

BETTER THINGS FOR BETTER LIVING...THROUGH CHEMISTRY



KEEPS WHITE FOOTWEAR WHITE

Sun Rubber-Process Aid Solves Costly Discoloration Problem

White rubber footwear discolored in use and colored sportswear soles bled into the white finishing tape. In trying to solve this serious problem, a large rubber manufacturer experimented with 12 specially selected process aids. Only two were successful: a Sun product and one much more expensive.

The Sun process aid was chosen and has proved completely satisfactory. Used to wet pigments, to soften rubber stocks, to smooth calendering, and to aid plasticizing, it causes neither staining nor discoloration. In fact, the white stocks treated with the Sun product retain their whiteness as long as control stocks containing no processing aid at all.

Sun rubber-process aids speed up milling and calendering; minimize bleeding and migrating; reduce flex-cracking, heat build-up, and hardening. Also they generally increase the resilience of the finished vulcanizate. Sun "Job Proved" process aids are refined for maximum compatibility with the types of rubber for which they are recommended —natural, synthetic, or reclaim.

To learn how Sun rubber-process aids may help you, call the nearest Sun Office. The services of a Sun representative are available without obligation.

SUN OIL COMPANY • *Phila. 3, Pa.*

In Canada: Sun Oil Company, Ltd.—Toronto and Montreal

SUN PETROLEUM PRODUCTS

"JOB PROVED" IN EVERY INDUSTRY

SUNOCO

RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XXIII NUMBER 4

October-December, 1950

Published under the Auspices of the
DIVISION OF RUBBER CHEMISTRY
of the
AMERICAN CHEMICAL SOCIETY

CARBON BLACKS

for **RUBBER COMPOUNDING**

•

MPC (Medium Processing Channel)
STANDARD MICRONEX

•

EPC (Easy Processing Channel)
MICRONEX W-6

•

HAF (High Abrasion Furnace)
STATEX-R

•

FF (Fine Furnace)
STATEX-B

•

FEF (Fast Extruding Furnace)
STATEX-M

•

HMF (High Modulus Furnace)
STATEX-93

•

SRF (Semi-Reinforcing Furnace)
FURNEX

• COLUMBIAN COLLOIDS •

COLUMBIAN CARBON CO. • **BINNEY & SMITH CO.**
MANUFACTURER DISTRIBUTOR

400 TONS OF SMOKE A DAY

RUBBER CHEMISTRY AND TECHNOLOGY

Published quarterly under the Auspices of the Division of Rubber Chemistry of the American Chemical Society,
Prince and Lemon Streets,
Lancaster, Pa.

Editor ..... C. C. DAVIS
Advertising Manager ..... E. H. KRISMANN
Secretary ..... C. R. HAYNES
Treasurer ..... C. W. CHRISTENSEN

Vol. XXIII Oct.-Dec., 1950 No. 4

CONTENTS

General Section PAGE

Officers iii
Special Committees for 1949–1950 v
New Books and Other Publications vi

Papers

Thixotropic Behavior of Carbon Black in Rubber. L. MULLINS 733
Elongation Hysteresis of Hevea and Synthetic Elastomers. M. MOONEY AND S. A. BLACK 744
Low Temperature Behavior of Butadiene-Styrene Coploymers. Effect of Compounding Variables. R. D. JUVE AND J. W. MARSH 760
Low-Temperature Stiffening of Elastomers. S. D. GEHMAN, P. J. JONES, C. S. WILKINSON, JR., AND D. E. WOODFORD 770
Stress Relaxation of Some Rubber and Synthetic Rubber Vulcanizates in Compression. J. R. BEATTY AND A. E. JUVE 786
Mechanism of Reënforcement. III. Viscosity of Carbon Black Suspensions in GR-S Solutions. LEONARD E. AMBORSKI AND GEORGE GOLDFINGER 803
New Types of Highly Elastic Substances. Vulcollans. O. BAYER, E. MÜLLER, S. PETERSEN, H. F. PIEPENBRINK, AND E. WINDEMUTH 812
Oxidation of Compounds Structurally Related to GR-S. J. W. LAWRENCE AND J. REID SHELTON 836
Structure of Vulcanized Latex. N. C. HUMPHREYS AND W. C. WAKE 847
Oxidation Processes in Latex of Hevea Brasiliensis. L. N. S. DE HAAN-HOMANS 858
Vulcanization of Neoprene Type W. D. B. FORMAN, R. R. RADCLIFF, AND L. R. MAYO 874
Use of Oxidizing Agents in Rubber Vulcanization. Zinc Oxide-Free Process. BERNARD C. BARTON 888

The Use of Zinc Dibutyldithiocarbamate in the Manufacture of Cellular Rubber. ADRIEN HAEHL 897

Stability of Crude GR-S. Effect of Traces of Antioxidant. E. J. GLAZER, C. R. PARKS, J. O. COLE, AND J. D. D'IANNI 905

The Evaluation of Flex-Life and Heat Build-Up Properties of Elastomers. E. B. STOREY 910

Dynamic Compression Test for Adhesion of Rubber to Cord Fabric. G. A. PITTMAN AND E. R. THORNLEY 921

Tack of Butyl and Natural Rubbers. R. K. BECKWITH, L. M. WELCH, AND J. F. NELSON 933

Rubber Bonding. J. M. BUIST AND W. J. S. NAUNTON 945

Determination of Copper in Raw Materials Used in the Rubber Industry. J. GENOVA AND A. ADDOBBATI 972

Polarographic Determination of Zinc in Compounded Rubber. F. C. J. POULTON AND L. TARRANT 975

Mechanical Stability Test for Hevea Latex. H. G. DAWSON 981

RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

RUBBER CHEMISTRY AND TECHNOLOGY may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Division of Rubber Chemistry by payment of the dues ($2.50 per year) to the Division and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.

(2) Anyone who is not a member of the American Chemical Society may become an Associate of the Division of Rubber Chemistry upon payment of $5.00 per year to the Treasurer of the Division of Rubber Chemistry, and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.

(3) Companies and libraries may subscribe to RUBBER CHEMISTRY AND TECHNOLOGY at the subscription price of $5.00 per year.

To these charges of $2.50 and $5.00, respectively, per year, postage of $.20 per year must be added for subscribers in Canada, and $.50 per year for those in all other countries not United States possessions.

All applications for regular or for associate membership in the Division of Rubber Chemistry with the privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, missing numbers, and all other information or questions should be directed to the Treasurer of the Division of Rubber Chemistry, C. W. Christensen, Monsanto Chemical Company, 920 Brown St., Akron, Ohio.

Articles, including translations and their illustrations, may be reprinted if due credit is given RUBBER CHEMISTRY AND TECHNOLOGY.

THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY

OFFICERS AND EXECUTIVE COMMITTEE

Chairman.....J. H. FIELDING, Armstrong Rubber Co., West Haven, Conn.
Vice-Chairman.....W. L. SEMON, B. F. Goodrich Co., Akron, Ohio
Secretary.....C. R. HAYNES, Binney & Smith Co., New York, N. Y.
Treasurer.....C. W. CHRISTENSEN, Monsanto Chemical Co., Akron, Ohio
Directors.....F. W. STAVELY (Past Chairman), C. C. DAVIS (Editor of *Rubber Chemistry and Technology*), E. H. KRISMANN (Advertising Manager of *Rubber Chemistry and Technology*), W. J. SPARKS (Director-at-Large); (regional group representatives for two years) H. F. PALMER (Akron), J. C. WALTON (Boston), E. C. SIVERSON (Buffalo), F. S. FROST, JR. (Chicago), R. E. BITTER (Los Angeles), M. R. BUFFINGTON (New York); (regional group representatives for one year) W. J. O'BRIEN (Connecticut), G. P. HOLLINGSWORTH (Detroit), G. S. RAMSEY (Northern California), R. A. KURTZ (Philadelphia), E. L. HANNA (Rhode Island), R. A. CLARK (Southern Ohio), NORMAN BEKKEDAHL (Washington, D. C.).

OFFICERS OF LOCAL GROUPS

AKRON

Chairman....E. L. STANGOR, E. I. duPont de Nemours & Co., 40 E. Buchtel Ave., Akron 8, Ohio. *Vice-Chairman*....D. F. BEHNEY, Harwick Standard Chemical Co., 60 S. Seiberling St., Akron 3, Ohio. *Secretary*.... L. M. BAKER, The General Tire & Rubber Co., Akron Ohio. *Treasurer*.... R. D. JUVE, The Mohawk Rubber Co., 1235 Second St., Akron, Ohio.

• • • • • •

BOSTON

Chairman....H. W. SUTTON, Boston Woven Hose & Rubber Co., Cambridge, Mass. *Vice-Chairman*....T. C. EDWARDS, Acushnet Process Co., New Bedford, Mass. *Secretary-Treasurer*....JOHN ANDREWS, Godfrey L. Cabot Co., 77 Franklin St., Boston, Mass. (Terms expire December, 1950).

• • • • • •

BUFFALO

Chairman....J. G. AUGENSTEIN, U. S. Rubber Reclaiming Co., Buffalo, N. Y. *Vice-Chairman*....P. H. TUFTS, 219 Roycroft Boulevard, Snyder, N. Y. *Secretary-Treasurer*....OREN FERSTER, Queen City Rubber Co., Buffalo, N. Y. (Expiration of terms not announced).

• • • • • •

Chicago

Chairman....P. F. Niessen, Victor Manufacturing & Gasket Co., Chicago, Ill. *Vice-Chairman*....J. F. Taylor, Commercial Solvents Corp., Chicago, Ill. *Secretary-Treasurer*....J. E. A. Hopkins, Van Cleef Brothers, Chicago, Ill. (Terms expire in 1951).

• • • • • •

Connecticut

Chairman....D. F. Spengler, Sponge Rubber Products Co., Derby, Conn. *Vice-Chairman*....C. A. Larson, Whitney Blake Co., Hamden, Conn. *Secretary*....G. R. Sprague, Sponge Rubber Products Co., Derby, Conn. *Treasurer*....F. Rooney, General Electric Co., Bridgeport, Conn. (Terms expire in fall of 1950).

• • • • • •

Detroit

Chairman....G. M. Wolf, Sharples Chemicals, Inc., Detroit, Mich. *Vice-Chairman*....G. T. Lindner, Minnesota Mining & Manufacturing Co., Detroit, Mich. *Secretary*....E. V. Hindle, U. S. Rubber Co., Detroit, Mich. *Treasurer*....E. J. Kvet, Baldwin Rubber Co., Pontiac, Mich. (Terms expire December 1950).

• • • • • •

Los Angeles

Chairman....E. C. McLaughlin, H. M. Royal Co., Los Angeles, Calif. *Associate Chairman*....R. D. Abbott, R. D. Abbott Co., Los Angeles, Calif. *Vice-Chairman*....R. L. Short, Kirkhill Rubber Co., Los Angeles, Calif. *Secretary*....C. S. Hoglund, Goodyear Tire & Rubber Co., Los Angeles, Calif. *Treasurer*....L. E. Budnick, Ohio Rubber Co., Long Beach, Calif. (Terms expire December, 1950).

• • • • • •

New York

Chairman....D. E. Jones, American Hard Rubber Co., Butler, N. J. *Vice-Chairman*....H. G. Ling, Naugatuck Chemical Division, U. S. Rubber Co., New York, N. Y. *Secretary-Treasurer*....Peter P. Pinto, *The Rubber Age*, 250 W. 57th St., New York, N. Y. (Terms expire December, 1950).

• • • • • •

Northern California

Chairman....F. W. Swain, Pioneer Rubber Mills, Pittsburg, Calif. *Vice-Chairman*....R. R. James, Mare Island Naval Shipyard, Vallejo, Calif. *Secretary*....J. F. Mason, Pioneer Rubber Mills, Pittsburg, Calif. *Treasurer*....G. S. Ramsey, Grove Regulator Co., Emeryville, Calif. (Terms expire December, 1950).

• • • • • •

Philadelphia

Chairman....T. J. Gorman, Quaker Rubber Corp., Philadelphia, Penna. *Vice-Chairman*....H. J. Reid, L. H. Gilmer Co., Division of U. S. Rubber Co.,

Philadelphia, Penna. *Secretary-Treasurer*....T. W. ELKINS, Armstrong Cork Co., Lancaster, Penna. (Expiration of terms not announced).

• • • • • • •

RHODE ISLAND

Chairman....F. S. BARTLETT, U. S. Rubber Co., Bristol, R. I. *Vice-Chairman*....F. V. NEWMAN, Respro, Inc., Cranston, R. I. *Secretary-Treasurer*....C. L. KINGSFORD, Davol Rubber Co., Providence, R. I. (Terms expire November, 1950).

• • • • • • •

SOUTHERN OHIO

Chairman....R. B. SUCHER, Inland Manufacturing Division, General Motors Corp., Dayton, Ohio. *Vice-Chairman*....L. J. KEYES, Dayton Rubber Co., Dayton, Ohio. *Secretary*....R. HOSKIN, Inland Manufacturing Division, General Motors Corp., Dayton, Ohio. *Treasurer*....T. C. ARGUE, Inland Manufacturing Division, General Motors Corp., Dayton, Ohio. (Terms expire December, 1950).

• • • • • • •

WASHINGTON

Chairman....WARREN STUBBLEBINE, Office of the Quartermaster-General, Dept. of the Army, Washington, D. C. *Vice-Chairman*....T. R. SCANLAN, Gates Rubber Co., Washington, D. C. *Secretary*....R. E. HARMON, Connecticut Hard Rubber Co., Washington, D. C. *Treasurer*....E. G. HOLT, Office of Domestic Commerce, U. S. Dept. of Commerce, Washington, D. C. *Recording Secretary*....(Miss) ETHEL LEVENE, Bureau of Ships, U. S. Navy Dept., Washington, D. C. (Terms expire October 1951).

• • • • • • •

SPECIAL COMMITTEES FOR 1949–1950

Auditing—E. H. KRISMANN (Chairman), O. D. COLE, H. F. PALMER.

Bibliography—(*Policy*) J. MCGAVACK (Chairman), C. W. CHRISTENSEN, C. C. DAVIS, M. E. LERNER. (*Editorial*) V. L. BURGER, D. E. CABLE, T. L. WILSON.

Councilors—S. G. BYAM, H. E. OUTCAULT (*Alternates*, A. M. NEAL, J. C. WALTON).

File and Records—J. D. D'IANNI (Chairman), R. B. APPLEBY, DOROTHY HAMLEN, A. M. NEAL.

Finance and Budget—C. P. HALL (Chairman), J. M. BIERER, H. L. TRUMBULL.

Liaison—J. H. FIELDING (Chairman), J. E. FELDMAN, C. E. FRICK, R. E. HUTCHINSON, F. H. SPRINGER.

Library—B. S. GARVEY, JR. (Chairman), R. B. APPLEBY, FERN BLOOM, LOIS BROCK, DORRIS HALL, DOROTHY HAMLEN, H. E. SIMMONS, H. N. STEVENS, LEORA STRAKA, H. C. TINGEY.

Membership—L. V. COOPER (Chairman). *Akron*—K. R. GARVICK, Firestone Tire & Rubber Co.; LYNN HARBISON, Phillips Petroleum Co.; M. H. LEONARD, Binney & Smith Co.; J. A. MERRILL, Goodyear Tire & Rubber Co.; D. V. SARBACH, B. F. Goodrich Co.; H. S. SELL, B. F. Goodrich Research

Center; Ross Shearer, B. F. Goodrich Research Center. *Boston*—B. H. Capen, Tyer Rubber Co.; T. M. Knowland, Boston Woven Hose & Rubber Co.; L. L. Longworth, Monsanto Chemical Co.; J. A. Mackay, Phillips Petroleum Co.; J. A. Williams, Haartz-Mason, Inc.. *Chicago*—R. L. Campbell, New Jersey Zinc Sales Co.; R. E. Elliott, Indol Chemical Co.; J. S. Harrison, Witco Chemical Co.; R. O. Hartman, Monsanto Chemical Co.; A. E. Lawrence, Phillips Petroleum Co.; W. H. Lussie, R. T. Vanderbilt Co.; R. K. Opper, Naugatuck Chemical Division; P. L. Sheppard, Armour & Co. *Detroit*—G. R. Cuthbertson, U. S. Rubber Co.; E. J. Kvet, Baldwin Rubber Co.; G. F. Lindner, Minnesota Mining & Manufacturing Co.; W. J. Simpson, Chrysler Corp.; G. M. Wolf, Sharples Chemicals, Inc. *Los Angeles*—A. W. Bartell, U. S. Rubber Co.; H. A. Beeson, B. F. Goodrich Co.; R. T. Hickox, Goodyear Tire & Rubber Co.; R. E. Hutchinson, Firestone Tire & Rubber Co.; D. C. Maddy, Harwick Standard Chemical Co. *New York*—G. N. Vacca, Bell Telephone Laboratories, Inc. *Northern California*—A. E. Barrett, U. S. Naval Rubber Laboratory. *Philadelphia*—H. J. Reid, L. H. Gilmer Co. *Rhode Island*—Charles Berlow, Berlow & Schlosser; E. L. Hanna, Davol Rubber Co.; Harry Schlosser, Berlow & Schlosser; F. H. Springer, Davol Rubber Co. *Southern Ohio*—R. A. Clark, Battle Institute; J. E. Feldman, Inland Manufacturing Division, General Motors Corp., H. R. Gill, Goodyear Tire & Rubber Co. *Washington*—J. T. Cox, Jr., Russell & Gordon McBride.

Nominating—S. M. Cadwell (Chairman), J. G. Augenstein, H. I. Cramer, N. A. Shepard, W. W. Vogt.

Papers Review—C. C. Davis, J. H. Fielding, C. R. Haynes.

Program—G. H. Swart (Chairman), A. M. Clifford, A. E. Juve, G. E. P. Smith, Jr., A. W. White.

Teller—R. W. Kixmiller (Chairman), E. B. Curtis, A. R. Davis.

NEW BOOKS AND OTHER PUBLICATIONS

Elastomers and Plastomers; Their Chemistry, Physics, and Technology. Volume I. General Theory. Edited by R. Houwink. Elsevier Publishing Co., Inc., 215 Fourth Ave., New York 3, N. Y. Cloth, 6¾ by 10 inches, 509 pages. Price, $7.—This volume, the last to be published, completes the series of three books; Volume II covered manufacture, properties, and applications; Volume III covered testing and analysis, and tabulation of properties. Volume I provides a wealth of information on theoretical aspects of high polymer chemistry and physics. There are ten chapters contributed by authorities in the field, and each chapter includes an extensive bibliography of references. Although the latest references are in 1948, the value of this work, particularly in combination with the other two volumes, will be evident to all students in the field of high polymers.

Chapters and their contributors follow: "Economic Aspects", H. A. Frank; "Organic Chemistry", C. Koningsberger; "Reaction Kinetics and Mechanism of Polyreactions", H. Wechsler, W. P. Hohenstein, and H. Mark; "Molecular Constitution", "Mechanical Properties", "Physics and Structure", G. J. van Amerongen; "Electrophysics", L. Hartshorn; "Mechanical Operations", H. Gibello; "Polymer-Liquid Interaction", van Amerongen; and "Plasticizers", R. S. Colborne. [From the *India Rubber World.*]

STANDARDS ON RUBBER PRODUCTS: 1950. Published by the American Society for Testing Materials, 1916 Race St., Philadelphia 3, Penna. 6 × 9 in. 652 pp. $4.75.—This latest edition of A.S.T.M. standards, issued through the work of Committee D-11 on Rubber and Rubberlike Products, includes all the standard and tentative test methods and specifications pertaining to rubber products. An idea of the coverage of the rubber standards can be had from the following list, the number of standards applicable being indicated in the parentheses: Processibility Tests (3), Chemical Tests of Vulcanized Rubber (4), Physical Tests of Vulcanized Rubber (21), Aging and Weathering Tests (8), Low Temperature Tests (5), Automotive and Aeronautical Rubber (7), Hose and Belting (5), Tape (3), Electrical Protective Equipment (6), Rubber-Coated Fabrics (3), Insulated Wire and Cable (13), Hard Rubber (3), Latex Foam, Sponge and Expanded Cellular Rubber (2), Rubber Cements (2), Rubber Latices (2), Packing Materials (2), Non-Rigid Plastics (10), Electrical Tests (4), Nomenclature and Definitions (4). Many of the specifications and tests included have been reviewed recently by the society. [From *The Rubber Age* of New York.]

L'INSTITUT FRANÇAIS DU CAOUTCHOUC ET L'INSTITUT DES RECHERCHES SUR LE CAOUTCHOUC EN INODCHINE. (THE FRENCH RUBBER INSTITUTE AND THE RUBBER RESEARCH INSTITUTE IN INDO-CHINA). French Rubber Institute, 42 Rue Scheffer, Paris 16-e, France. 8½ × 10¾ in. 40 pp.—The history of both the French Rubber Institute, organized in 1936 in the laboratories of the French College of Organic Chemistry and moved into its own building in Paris in 1939, and the Rubber Research Institute in Indo-China, organized in 1940, is given in this booklet. The aims, objectives and achievements to date of both organizations, which are closely interrelated, are discussed, and the testing equipment in both laboratories is illustrated in large, full-page reproductions. A complete list of the publications issued by the research groups, numbering over one hundred, is given. An outline map showing the method of administration pertaining to both organizations is appended to the booklet, indicating how their work is tied in with the Rubber Study Group, the International Rubber Development Committee, and other groups. [From *The Rubber Age* of New York.]

SYMPOSIUM ON EFFECTS OF LOW TEMPERATURES ON THE PROPERTIES OF MATERIALS. American Society for Testing Materials, 1916 Race St., Philadelphia 3, Penna. 6 × 9 in. 68 pp. $1.50.—The papers and discussion in this booklet were presented in two sessions at a meeting of the Philadelphia District of the A.S.T.M., in Philadelphia, March 19, 1946. It covers the fields of both ferrous and nonferrous metals, plastics and rubbers. Following an introduction by A. O. Schaefer, of the Midvale Co., the booklet contains four profusely illustrated papers, as follows: (1) Low Temperature Behavior of Organic Plastics, by H. K. Nason, T. S. Carswell, and C. H. Adams; (2) Low-Temperature Properties of Elastomers, by J. W. Liska; (3) Effects of Subatmospheric Temperatures on the Properties of Non-Ferrous Metals, by N. L. Mochel; (4) The Properties of Weldments at Low Temperatures, by R. D. Stout. [From *The Rubber Age* of New York.]

MANUAL ON FATIGUE TESTING. (Special Technical Publication No. 91). American Society for Testing Materials, 1916 Race Street, Philadelphia 3, Penna. 6 × 9 in. 82 pp. $2.50.—This new manual culminates several years

of work by A.S.T.M. Committee E-9 on Fatigue Testing. The purpose of the manual is to supply information to those setting up new laboratory facilities, to aid in operating the equipment properly, and to offer advice on presentation and interpretation of data. The manual contains eight sections, including the introduction (Section I). Section II on Symbols and Nomenclature for Fatigue Testing defines all terms, and their corresponding symbols, likely to be found in fatigue testing. The symbols are those recommended by the American Standards Association.

Section III on Fatigue Testing Machines classifies them as to type of load, type of stress, design characteristics, and operating characteristics. More than 30 illustrations aid in showing the differences in the various types of fatigue testing machines. This section contains a bibliography of more than 120 references. Specimens and Their Preparation are described in Section IV which presents information on various types of specimens, both metallic and nonmetallic, with detailed instructions for polishing.

Section V. on Test Procedure and Technique discusses such things as planning of tests, selection of fatigue machines, selection of samples and preparation, and measuring specimens. A special bibliography has 44 references. Section VI on Presentation of Fatigue Data and Section VII on Interpretation of Fatigue Data describe general consideration in presentation and interpretation of data obtained from three different types of tests designated as material type, structural type, and actual-service type. An extensive bibliography (Section VII), which contains more than 50 references, completes the publication. [From *The Rubber Age* of New York.]

Abstracts of Patents Relating to Rubber Latex. Vol. II. By T. R. Dawson and R. W. Parris. Published by the British Rubber Development Board, Market Buildings, Mark Lane, London, E.C. 3, England. $5\frac{1}{2} \times 8\frac{1}{2}$ in., 86 pp.—The fourth edition of "Rubber Latex", by H. P. Stevens and W. H. Stevens, published in 1936, contained a collection of 925 abstracts of British patents relating to latex, ending with British Patent No. 438,795. That collection of patents was supplemented by a further series of 1,052 abstracts, entitled "Abstracts of Patents Relating to Rubber Latex", published in 1941 and covering British patents 438,796 to 520,735. The present booklet is a further supplement of 427 abstracts, carrying the series through British patent 603,628, or the period from 1940 through 1948. Like the previous edition, the current one is limited to patents relating to Hevea latex and to artificial aqueous dispersions of Hevea rubber or reclaimed Hevea rubber. Name and subject indexes are included. [From *The Rubber Age* of New York.]

Standards on Electrical Insulating Materials: 1950. Published by the American Society for Testing Materials, 1916 Race St., Philadelphia 3, Penna. 6×9 in. 670 pp. $4.85.—Compiled by A.S.T.M. Committee D-9, this book includes all of the standard and tentative test methods and specifications pertaining to electrical insulating materials. Included are 16 standards for insulating fabrics and textile materials, 8 on rubber tape and electrical protective equipment, 5 on plastics, 11 on mineral oils, 6 on insulating shellac and varnish, 2 on solid filling and treating compounds, and 5 on insulating papers. Many of the specifications and tests have been revised recently by the society. [From *The Rubber Age* of New York.]

RUBBER IN AIRCRAFT. By T. L. Garner and J. F. Powell, Published by the British Rubber Development Board, Market Buildings, Mark Lane, London, E. C. 3, England. 5½ × 8½ in. 72 pp.—This is one of the most comprehensive treatises on the numerous applications of rubber in aircraft yet compiled. It contains ten chapters: (1) Rubber as an Engineering Material; (2) Rubber Processing; (3) Airplane Tires; (4) Deicing Equipment; (5) Hydraulic Applications and Oil Seals; (6) Insulation Suspension; (7) Hose and Tubing; (8) Fuel Tanks; (9) Miscellaneous Uses; (10) Conclusion. The booklet contains numerous photographs and schematic drawings, and also includes a list of suggested references for further reading. Its value is enhanced by the inclusion of a subject index. Copies are available without cost on written request to the British Rubber Development Board. [From *The Rubber Age* of new York.]

PHYSICAL CHEMISTRY OF HIGH POLYMERIC SYSTEMS. (Second Edition). By H. Mark and A. V. Tobolsky. Published by Interscience Publishers, Inc., 215 Fourth Ave., New York 3, N. Y. 6 × 9 in. 506 pp. $6.50.—So much progress has been made in most branches of polymer science since publication of the first edition of this work in 1940 that the authors deemed it advisable to expand and amend the text. Some indication as to how much progress has been made in the interim is given by the fact that this new edition, which has been completely revised, contains an additional 150 pages, 56 figures, and 13 tables. Like the first edition, the current work presents a condensed selection of the basic facts of the physical chemistry of macromolecules. The chapters on molecular structure are followed by a treatment of the present concept of intra-and intermolecular forces. Since the thermodynamic and kinematic behavior of polymer solutions and the mechanical properties of polymers have come under intensive investigation in the past ten years, the chapters on these subjects include far more detailed information than the corresponding chapters in the first edition. The book has 13 chapters, and author and subject indexes. [From *The Rubber Age* of New York.]

ADVANCES IN COLLOID SCIENCE: VOL. III. Edited by H. Mark and E. J. W. Verwey. Published by Interscience Publishers, Inc., 215 Fourth Ave., New York 3, N. Y. 6 × 9 in. 384 pp. $7.50.—This is the third in a series to provide a medium in which recent significant discoveries or advances in colloid science, either experimental or theoretical, would be presented in a comprehensive and unified fashion. Several of these developments were covered in the first volume issued in 1942. The second volume, issued in 1946, was devoted to a field of special and actual interest at that time, *i.e.*, the analysis and characterization of the rubbery state, the volume being subtitled "Scientific Progress in the Field of Rubber and Synthetic Elastomers". This third volume covers a series of topics and gives an approximate cross-section through those branches of colloid science that have grown rapidly or shown unexpected developments during the last few years. A fourth volume is in preparation.

The current work covers seven specific subjects, each prepared by experts in the field and complete with bibliographies. These subjects and their authors are: (1) Atomic Forces and Adsorption, by J. H. De Boer; (2) Surface Chemistry and Colloids, by A. E. Alexander; (3) Quantitative Interpretation of the Electrophoretic Velocity of Colloids, by J. Th. G. Overbeek; (4) Lyogels, by E. A. Hauser; (5) Ultracentrifugal Sedimentation of Polymolecular Substances, by Per-Olof Kinell and Bengt G. Ranby; (6) Fatigue Phenomena in High

Polymers, by J. H. Dillon; (7) Flotation, by Strathmore R. B. Cooke. A subject index is included. [From *The Rubber Age* of New York.]

CHEMICAL ENGINEERS' HANDBOOK. (Revised Third Edition.) Edited by John H. Perry. Published by McGraw-Hill Book Co., Inc., 330 West 42nd St., New York 18, N. Y. $7\frac{1}{4} \times 10$ in. 1942 pp. $15.00.—An authoritative group of more than 140 recognized specialists have contributed detailed explanations of new developments in every branch of industry to bring the latest edition of this standard chemical engineering reference work completely up to date. Full coverage of essential processes, equipment, materials, etc., is provided in some 30 complete sections. Several entirely new sections are incorporated, providing important information pertaining to furnaces and kilns, size enlargement, general theory of diffusional operations, etc. More than 2000 charts, diagrams, cross-sections, flow sheets, etc., are included, all drawings having been newly prepared and increased in size for greater clarity. All subject matter is arranged in two columns for greater legibility and an extensive index makes use of more common words and includes their synonymns and and equivalents. [From *The Rubber Age* of New York.]

THIXOTROPIC BEHAVIOR OF CARBON BLACK IN RUBBER *

L. MULLINS

RESEARCH ASSOCIATION OF BRITISH RUBBER MANUFACTURERS, 105 LANSDOWNE ROAD, CROYDON, SURREY, ENGLAND

INTRODUCTION

Solid fillers were first incorporated into rubber as diluents to cheapen the finished rubber products, but it was soon found that some fillers gave improved strength and serviceability when compared with pure rubber, and to these fillers the term reënforcing agents has been applied. It is now possible, by a suitable choice of fillers and other compounding ingredients, to produce rubbers with a whole range of desired physical properties. Carbon blacks are by far the most important fillers used in the rubber industry, and are the only ones capable of giving the highest degree of reënforcement; the carbon blacks used are of extremely fine particle size and range from the coarser lampblacks with average particle diameters of about 2000 Å. to very fine colloidal blacks with average particle diameters as small as 200 Å. Relatively large concentrations of black are often employed, and concentrations of 20 per cent by volume are usual.

Investigations into the behavior of concentrated dispersions of colloidal carbon black in oil or water have shown that this behavior is complex; often the dispersions possess thixotropic properties—if allowed to stand they may progressively increase in consistency, only to become more mobile during working[1]. Similar time-dependent thixotropic properties are observed in other systems, and it is almost invariably found that these systems possess some kind of internal structure, which is formed by interactions between the dispersed particles, and which in turn lead to flocculated aggregates. Breakdown and subsequent reformation of this structure are responsible for the thixotropic behavior of the system.

It has not been generally recognized that many of the physical properties of rubbers containing carbon black or other fine-particle fillers show evidence of similar thixotropic behavior, and in this paper we shall describe the influence of these effects on the properties of both vulcanized and unvulcanized rubbers and discuss their bearing on theories of the reënforcement of rubber by fillers.

EXPERIMENTAL INVESTIGATIONS

UNVULCANIZED RUBBER

Before vulcanization, rubber is a plastic material capable of being shaped and molded, and in this state it is its flow properties—viscosity or plasticity—which are of importance. A series of experiments on the effect of carbon blacks on the plasticity of rubber stocks, to be reported in detail elsewhere, has recently

* Reprinted from the *Journal of Physical and Colloid Chemistry*, Vol. 54, No. 2, pages 239–251, February 1950. This paper was presented at the Twenty-third National Colloid Symposium, held under the auspices of the Division of Colloid Chemistry of the American Chemical Society at Minneapolis, Minnesota, June 6–8, 1949.

been carried out by Mullins and Whorlow[2]. Work was confined to rubber stocks without vulcanizing ingredients to avoid complications due to vulcanization occurring during plasticity measurements. The measurements were made on the modified Mooney shearing disc plastimeter described by Piper and Scott[3]; this uses a biconical rotor to give a substantially uniform rate of shear throughout the rubber. Measurements were made of the torque required to shear rubber stocks, held at 100° C, at various rates of shear. The torque readings are given in arbitrary units; as a rough guide, 200 of these units correspond to a shear stress of 10^6 dynes per sq. cm.

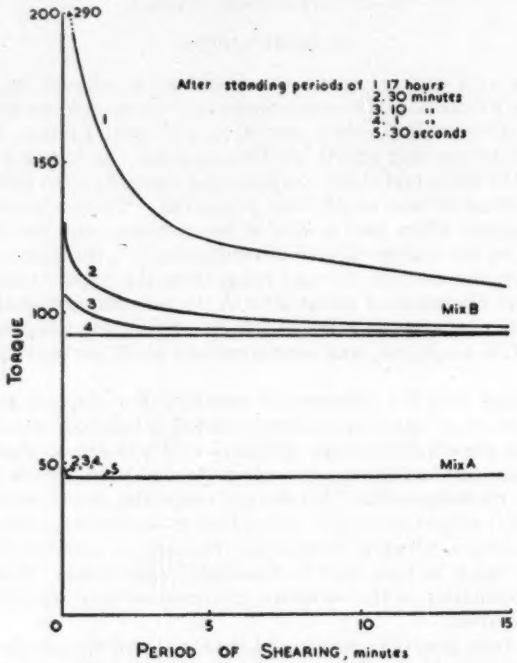


FIG. 1.—Typical families of torque-time curves determined during the continuous shearing of two rubber stocks.

Preliminary experiments showed that the rheological properties of the rubber stocks depended on the past history of the material; for example, their properties were changed continuously on the one hand by shearing and on the other hand by standing. Indeed, a wide range of values for the plasticity could be obtained, depending on this history and the conditions of test. Thus, to obtain reproducible measurements at any chosen shear rate, it was found necessary first to shear continuously for a relatively long period at a much higher rate of shear; this conditioning treatment brought the rubber stocks to a reproducible level where the behavior was substantially independent of differences in past history. This method was adopted throughout the investigations.

It was found that during standing at an elevated temperature, *e.g.*, 100° C, the rubber stocks grew progressively stiffer. Figure 1 shows typical families of

torque-time curves determined during the continuous shearing of two rubber stocks, a masticated smoke sheet (Mix A) and a carbon black stock containing 22 volumes of an M.P.C. black per 100 volumes of rubber (Mix B). The stocks had been previously brought to a reproducible level by shearing for 20 minutes at a shear rate of 10 sec.$^{-1}$, and measurements were subsequently made, after various periods of standing, at a shear rate of 1 sec.$^{-1}$. These curves show clearly the progressive increase in stiffness which occurs on standing; they also show a softening occurring during the continuous shearing of the stocks. This softening occurs rapidly at first and then more slowly, until an approximately steady value of the torque is attained.

It appears that at least two processes are taking place during the continuous shearing of rubber stocks: firstly, a growth in structure, which leads to an increase in the torque required to shear the material, and secondly, a breakdown in structure which causes a decrease in torque. The steady value of the torque is reached when the rate of growth equals the rate of breakdown, and it can be considered to be a state of dynamic equilibrium, less structure being present at equilibrium during shearing at higher rates, as at these rates the breakdown is more rapid.

Both the masticated smoked sheet and the black-loaded stocks show evidence of internal structure that can be either broken down or built up. The changes occurring in the smoked sheet are very small when compared with those in stocks containing carbon black; in smoked sheet the structure is weak, is readily broken down, and quickly reforms; on the other hand, the structure in black-loaded stocks is much stronger, is only slowly broken down by shearing, reforms continuously on standing, and may produce a manifold increase in stiffness. It appears that all important structural changes are due to the presence of fillers.

In cases where considerable structure was present, it was found that for short periods of shearing the amount of thixotropic breakdown occurring in loaded stocks was a function of the work done on the stock; that is, when the total work done on the stock was the same, the amount of breakdown was independent of how the work was applied, *e.g.*, rapid shearing for a short time or slow shearing for a long time. A simple relationship of this type no longer held if shearing took place at a very low rate, *i.e.*, over a very extended period, but this was not unexpected because standing at elevated temperatures besides producing a growth of structure also lessened the ability of the material to form structure subsequently. The approximately steady state to which reference has already been made is thus not a true equilibrium.

The growth of structure during standing can conveniently be represented by the change in torque required to shear the material after various periods of standing. Figure 2 shows the change in the torque (read after shearing for 1 minute) with period of standing at 100° C; the results were obtained on stocks which contained the same volume loading of a number of carbon blacks, together with a result obtained on masticated smoked sheet. All of the stocks had been mechanically conditioned, as described above, before the commencement of the period of standing. The steady value of torque after conditioning but before standing is greatest for Shawinigan and smallest for M.T. black, among the carbon blacks studied. Differences in this steady value of torque correspond to filler structure which has not been broken down by previous shearing (conditioning) at 10 sec.$^{-1}$, the Shawinigan black showing the greatest amount of this "permanent" structure. The shapes of the curves also show pronounced differences; both the Shawinigan and the M.T. black show little

growth of structure during standing. It thus appears that the Shawinigan black has a strong structure, which is not easily broken down by shearing and which shows little growth on standing; the M.T. black shows little structure at all. On the other hand, the M.P.C. and U.F. blacks have a structure, which is broken down by shearing and reforms on standing; indeed, after long periods of standing the structure in these stocks exceeds that in the Shawinigan black stocks.

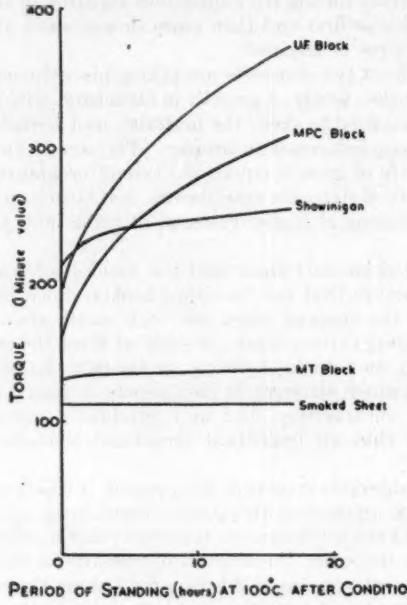


FIG. 2.—Change in torque with period of standing at 100° C.

The ability of the stocks to form structure is decreased by storage at elevated temperatures before the commencement of the mechanical conditioning treatment and subsequent standing; it may also be profoundly influenced by the addition of small quantities of surface-active materials.

VULCANIZED RUBBER

Similar thixotropic behavior is observed in vulcanized rubber. Probably the most popular physical test on vulcanized rubber is a tensile stress-strain test. Results showing the effect of previous stretching on the tensile properties of rubber have been discussed by the author elsewhere[4]; here it was shown that the shapes of stress-strain curves are not reproducible, but change with each successive deformation. Pure-gum vulcanizates without fillers are only slightly affected by previous stretching. On the other hand, vulcanizates containing fillers (such as carbon black) which stiffen the rubber may be considerably softer on second stretching, the original increase in stiffness produced by these fillers being largely destroyed at elongations less than the maximum elongation of previous stretch. Figure 3 shows typical results obtained on a natural rubber

vulcanizate containing 28 volumes of M.P.C. black to 100 volumes of rubber; it gives stress-strain curves for samples which had been (1) not previously stretched, (2) previously stretched to 280 per cent, and (3) previously stretched to the breaking elongation. A pure gum vulcanizate (without fillers) is given for comparison.

This softening is attributed to a breakdown of filler structure, and the degree of breakdown is greater, the greater the stiffening effect of the filler. The major portion of the relaxation of stress which occurs in strongly reënforced vulcanizates held at constant strain at normal temperature was also shown to be due

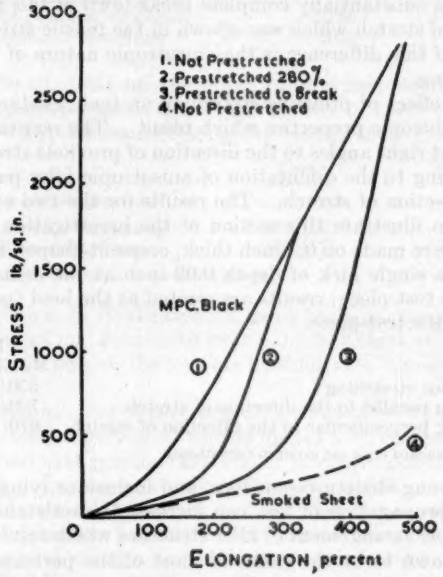


FIG. 3.—Typical results obtained on a natural-rubber vulcanizate containing 28 volumes of M.P.C. black per 100 volumes of rubber.

to a breakdown of filler structure. Although stretching produces a softening in all directions throughout the rubber, the degree of softening is not the same in all directions, but is greatest in the direction of stretch, so anisotropic stress-strain properties result from previous stretching. After breakdown the structure tends to reform, but for most practical purposes the softening can be considered permanent, as the regrowth of structure is slow at normal temperatures, and although it is more rapid at high temperatures, it appears that once a loaded vulcanizate has been used, it will probably never completely return to its initial state.

These results immediately raised questions about the effect of such treatment on other physical properties of vulcanized rubber.

In just the same way that the modulus of rubbers is affected by stretching, the hardness is also sensitive to previous history. The hardness of both the pure-gum and the M.P.C. black vulcanizate before and after previous stretching to their breaking elongation is given below. Here the hardness is quoted as the indentation in hundredths of a millimeter[5]. These results clearly show that

previous stretching leads to a considerable softening of the black vulcanizate and a slight softening of the unloaded vulcanizate, and so demonstrate the breakdown of some of the increased stiffness which results from the inclusion of carbon

	Before stretching	After stretching
M.P.C. black-loaded vulcanizate	36	66
Pure-gum vulcanizate	143	154

black. It is of interest to note that, even after previous stretching, the loaded vulcanizate is still considerably harder than the unloaded one; this should be contrasted with a substantially complete breakdown of this increased stiffness in the direction of stretch which was shown in the tensile stress-strain test. A possible source of this difference is the anisotropic nature of the stiffness after previous stretching.

Tests on the effect of previous stretching on tear resistance also show evidence of the anisotropic properties which result. The resistance to the propagation of a tear at right angles to the direction of previous stretch may actually be increased, owing to the orientation of anisotropic filler particles or particle chains in the direction of stretch. The results for the two vulcanizates which are being used to illustrate this section of the investigation are given below. Measurements were made on 0.1 inch thick, crescent-shaped test-pieces[6], which had been given a single nick of depth 0.02 inch at the center of the concave inner edge of the test-piece; results are quoted as the load (per inch thickness) required to tear the test-piece.

	Load in pounds	
	M.P.C. black	Pure gum
Without previous stretching	550(15)*	250(16)*
After stretching parallel to the direction of stretch	790(40)	280(18)
After stretching perpendicular to the direction of stretch	670(15)	260(16)

* Figures for the standard error are given in parentheses.

Tearing is strong structure-sensitive, and inclusions lying perpendicular to the direction of propagation of tear can increase the resistance to tearing.

The anisotropic arrangement of filler structure which results from stretching has also been shown to be the cause of most of the permanent set in all but grossly undercured vulcanizates[7]. This residual extension which remains after previous stretching is due to the incomplete recovery of anisotropic filler particles or particle chains which have been oriented in the direction of stretching. Fillers which have anisotropic particles or which readily form chains of particles show greater set than fillers with spherical particles.

Hysteresis properties of rubber vulcanizates are also affected by previous history, and with rubbers containing fillers a considerable amount of energy may have to be expended to break down filler structure during a cycle of deformation. The resilient energy or work required to rupture a sample of rubber in a simple tensile test has been widely used as an index of the quality of the rubber; and the difference between the resilient energies of loaded and unloaded vulcanizates, the ΔA function of Wiegand[8], is used as a criterion of the reënforcement produced by the filler. It has been usual to determine resilient energies from initial stress-strain curves, but it is now obvious that the values obtained in this way may vary considerably with the mechanical and thermal history of the material. The results in Table 1, determined before and after previous stretching to the breaking elongation, show that whereas previous stretching has only a small effect on the resilient energy of the pure-gum vulcanizate, the increase in resilient energy produced by the incorporation of M.P.C. black is

substantially destroyed by previous stretching. Thus the use of this property as an index of reënforcement is not recommended, as it may be quite misleading.

TABLE 1

	Resilient energy lb. per cu. in.	ΔA lb. per cu. in.
M.P.C. black-loaded vulcanizate		
Without previous stretching	5780	3030
After previous stretching	3020	370
Pure gum vulcanizate		
Without previous stretching	2750	
After previous stretching	2650	

On the other hand, tests on the effect of previous stretching on tensile strength and abrasion resistance show that neither of these properties is significantly altered. Typical resulsts are given below; those for abrasion resistance were obtained on a du Pont machine, using built-up samples, the abraded surface being that of a 2 cm. square cut from a 0.1 inch thick sheet. After completion of a running-in period, the volume loss during a 1-minute test run was determined.

M.P.C. black-loaded vulcanizate	Tensile strength lb. per sq. in.	Volume loss per hour cc.
Without previous stretching	2820(53)*	6.5(0.4)
After previous stretching	2880(57)	6.9(0.4)

* Figures for the standard error are given in parentheses.

There have been a number of investigations which record thixotropic effects shown by the electrical properties of rubbers loaded with carbon black[9]. There it has been recognized that previous thermal or mechanical treatment may profoundly affect such properties as conductivity, permittivity, and power factor. These results are of particular interest, as they show the existence of coherent contacting chains of carbon particles, these chains being disrupted by both mechanical and thermal changes and reforming again on standing.

The results quoted here to illustrate the behavior of vulcanized rubbers were obtained on two vulcanizates, one a pure gum and the other a M.P.C. black vulcanizate; in all cases when other vulcanizates containing various furnace, channel, and thermal blacks were investigated, the differences observed were only ones of detail. Fine channel and furnace blacks showed large thixotropic structural effects, whereas thermal blacks with relatively large particles showed little evidence of this type of structure.

DISCUSSION OF RESULTS

The results that have been described show clearly that in all rubbers, whether vulcanized or unvulcanized, there is some kind of internal structure which can be broken down by mechanical treatment and which forms again on standing. In rubber free from fillers, this structure breakdown is relatively small and can be accounted for by a disentanglement and orientation of the long-chain rubber molecules; these readjustments result in softening, and on standing thermal motion of the molecules allows them to return to the more probable entangled configuration. In rubbers containing fillers, the softening and stiffening due to structural changes may be much more pronounced, and the amount of structure which can be built up or broken down in this way depends

on the nature of the fillers. In this case an additional process involving the formation or breakdown of interactions between neighboring filler particles or between filler particles and rubber is responsible for this behavior.

As yet there is a serious lack of data on the exact nature of this structure, and no clear theoretical basis for relating internal structure with mechanical properties. Any theory which attempts to describe the effect of fillers on the physical properties of rubber must take into account these thixotropic phenomena. Here the main problem is to predict the behavior of the material from a knowledge of its past history. It will be recognized that this task is difficult even in the simplest case when all the structural changes are completely reversible, and that with loaded rubbers, where some irreversible structural changes also take place, the task is extremely complex.

There are obvious difficulties in the measurement of the physical properties of any thixotropic system. The measured values depend on the past history of the system, on both the magnitude and the duration of stresses which have been previously applied, and on the time of recovery which has elapsed since their removal; in addition, they are sensitive to temperature. In general, the properties of such systems are also altered by the act of measurement; thus any of a wide range of values can be obtained, depending on the history of the material and conditions of test. These difficulties can be overcome by using a standard instrument operating under closely controlled conditions, the usefulness of the results being determined by how well these conditions line up with working conditions, but before any data can be put to practical use the first essential is that they should be reproducible. The implications of the thixotropic behavior of rubber stocks and vulcanizates have not yet been fully recognized in the rubber industry, and it is clear that ideas on a number of popular tests require drastic revision,—in particular, tests of plasticity, stiffness, and hardness.

There are a number of suggested modifications which can usefully be put forward at this stage. Probably the most important practical consequence in the measurement of any property which is sensitive to previous history is that it is important that either the complete history of the rubber should be closely controlled, or the rubber should be conditioned before measurement so that its properties are substantially independent of differences in previous history. This latter course may not always be possible if samples differ considerably in history. If neither of these two conditions is satisfied, the results obtained may be completely misleading and certainly not capable of providing maximum information. The relative merits of these alternative methods of ensuring reproducibility depend on the use to which the results are to be put, and careful consideration must be given to details of any conditioning treatment adopted.

It will be recognized that conditioning only brings the material to an arbitrary reference level and that, although comparative results will be obtained on samples of different materials which have had similar conditioning treatments, the ratings of the materials may be very different for different types of conditioning. An example of this has already been mentioned during consideration of the results of plasticity measurements. If both the conditioning and the measurement involve little breakdown of structure, the results will be of little use in forecasting the likely behavior of the material under conditions which involve more severe deformations. If results are to be useful for design purposes, it is obviously essential that the material should have been previously deformed at least as severely as it is likely to be in service.

THEORIES OF REENFORCEMENT

We can now review current theories of the reënforcement of rubber produced by fillers. The term reënforcement has been applied to the improvement of almost any mechanical property which results from the addition of fillers, but it is now generally accepted that the improvement of any one property such as stiffness, tensile strength, tear strength, abrasion resistance, etc. does not mean that the rubber has been reënforced. Parkinson[10], for example, has suggested that a filler should not be classed as reënforcing unless it substantially improves both abrasion and tear resistance.

As the tensile stress-strain test has been the most popular physical test for vulcanized rubbers, it is not unnatural that results of tensile tests should have been widely used to give comparisons of the reënforcing ability of different fillers, and all of the socalled theories of reënforcement have been theories of the stiffening action of fillers. Here the possibility of using theories which have been developed to account for the viscosity of suspensions has attracted considerable attention. The basic theory developed by Einstein[11] describes the behavior of hard spherical noninteracting particles in a liquid which wets them completely, and considers only small volume concentrations. This theory has been extended to allow for higher concentrations, where interactions occur between neighboring particles and also to allow for nonspherical particles[12]. Guth and Gold have shown fair agreement between their modification of Einstein's theory and experiment up to volume concentrations as high as 25 per cent; for spherical particles they show that the viscosity η and the volume concentration c are related by the equation:

$$\eta = (1 + 2.5c + 14.1c^2)$$

while for rod-shaped particles the relationship is modified to:

$$\eta = \eta_0 (1 + 0.67fc + 1.62fc^2)$$

where the form factor f is the ratio of the length and breadth of the particles. Vand[13] has obtained an alternative formula which he shows is in good agreement with experimental results.

Smallwood[14], Rehner[15], and Guth[16] have all employed equations of this type to account for the increase in stiffness or change in flow properties which result from the incorporation of fillers into rubber, and more recently Cohan[17] has provided a considerable amount of experimental data which he claims supports the use of these equations. Smallwood recognized the need to condition his samples mechanically by previous stretching to high elongations to get reproducible results, and Guth in his earlier work describes a conditioning procedure; however, more recently Guth[18] and Cohan[19] have reported experimental work which does not fully appreciate the need to condition samples, and the very large thixotropic effects which we have shown are present in many measurements on both vulcanized and unvulcanized rubbers. Thus it appears that the reported agreement between theory and experiment must in some cases be fortuitous. Furthermore, changes in the shape of assemblies of filler particles which result from thermal or mechanical treatment of the rubber are presumably considerable, and thus a single valued form factor to describe the shape of assemblies of filler particles is not usually justified. In addition, it must not be forgotten that the conditions existing in the rubber-filler system and those assumed in the theory may be very different, and thus the validity of the formulas

that have been put forward should be checked and their limitations recognized before any further endeavor is made to use them to account for the behavior in our complex rubber-filled system[20]. It appears that the increase in stiffness which results from the incorporation of fillers is often merely an indication of the ability of the filler to form a thixotropic internal structure, and as this structure is sensitive to previous history it cannot be recommended as a suitable index to characterize the increased quality (reënforcement) of rubbers which results from incorporation of fillers.

There have been numerous discussions on the important features of fillers which govern their effect on the physical properties of rubber[21]. The size and shape of the filler particles, the chemical nature and structure of their particles, and particle surfaces have all been shown to be important. However, it appears that particle size is the primary factor influencing the reënforcing action of a filler, the finer particle fillers showing greater reënforcement. Of all the available fillers, carbon blacks have the finest particle size, and this probably accounts for much of their importance as reënforcing fillers for rubber. Electron-microscope studies show that carbon blacks of finer particle size form strong primary aggregates which are difficult to breakdown by mechanical means, and this investigation shows that, when fine particle blacks are compounded with rubber, they form a structure which can readily be broken down or built up, and which is associated with the formation of weak secondary aggregates of the filler particles or of those primary aggregates which have not been broken down by milling. It is interesting to note that properties which are now normally associated with reënforcement—such as tensile strength, tear resistance, and abrasion resistance—are unaffected by previous deformation, and thus the presence of secondary aggregates is not essential for reënforcement.

SUMMARY

The addition of carbon black may cause considerable changes in the physical properties of rubber. Often rubbers compounded with carbon black or other fillers show evidence of thixotropic behavior—their properties depend on the past history of the rubber and may be changed on the one hand by continuous standing and on the other hand by working. This paper describes investigations into the behavior of both unvulcanized and vulcanized rubbers, and discusses the thixotropic build-up and breakdown of colloidal carbon black structures which are shown to exist in rubber. The importance of this build-up and breakdown of structure has not been adequately appreciated in many measurements on compounded rubbers; for example, the terms viscosity, plasticity, and stiffness (modulus) can only be defined when complications due to thixotropy are carefully controlled before and during the actual measurement. A knowledge and understanding of this behavior enables the significance of the results of various tests on these materials to be more correctly assessed and accounts for behavior which has previously appeared to be anomalous. The deficiencies of earlier theories of the reënforcement of rubber produced by carbon black are indicated, and modifications which make allowance for thixotropic filler structure are proposed.

REFERENCES

[1] Arnold and Goodeve, *J. Phys. Chem.* 44, 652 (1940); Voet, *J. Phys. & Colloid Chem.* 51, 1037 (1947); Arnold, *J. Oil Colour Chem. Assoc.* 31, 237 (1948).
[2] Mullins and Whorlow, in press.
[3] Piper and Scott, *J. Sci. Instruments* 22, 206 (1945).
[4] Mullins, *J. Rubber Research* 16, 275 (1947).

[6] B. S. hardness number, B. S. 903–1940, p. 47.
[6] A.S.T.M. Designation D624-41T, die B.
[7] Mullins, *Proc. 2nd Rubber Technol. Conf.* (London), 1948, p. 179.
[8] Wiegand, *Ind. Eng. Chem.* 17, 939 (1925).
[9] Bulgin, *Trans. Inst. Rubber Ind.* 20, 24 (1944); Mullins, *J. Rubber Research* 16, 275 (1947); Wack, Anthony, and Guth, *J. Applied Physics* 18, 456 (1947); Parkinson and Blanchard, *Proc. 2nd Rubber Technol. Conf.* (London), 1948, p. 414.
[10] Parkinson, *Advances in Colloid Science* 2, 389 (1946).
[11] Einstein, *Ann. Physik* 19, 289 (1906); 34, 591 (1911).
[12] Guth and Gold, *Phys. Rev.* 53, 322 (1938); Eirich, *Repts. on Progress Physics* 7, 329 (1940).
[13] Vand, *J. Phys. Colloid Chem.* 52, 277 (1948).
[14] Smallwood, *J. Applied Physics* 15, 758 (1944).
[15] Rehner, *J. Applied Physics* 14, 638 (1943).
[16] Guth, *J. Applied Physics* 16, 20 (1945); *Proc. 2nd Rubber Technol. Conf.* (London), 1948, p. 353.
[17] Cohan, *India Rubber World* 117, 343 (1947); *Proc. 2nd Rubber Technol. Conf.* (London), 1948, p. 365.
[18] Guth, *Proc. 2nd Rubber Technol. Conf.* (London), 1948, p. 353.
[19] Cohan, *Proc. 2nd Rubber Technol. Conf.* (London), 1948, p. 365.
[20] The author has recently had the opportunity to see an as yet unpublished paper by S. G. Ward and H. L. Whittemore of Birmingham University, who have shown that, even though a very limited range, particle-size distribution may have a considerable effect on the viscosity of fairly concentrated dispersions of spherical particles.
[21] Parkinson, *Advances in Colloid Sci.* 2, 389 (1946); Cohan, *India Rubber World* 117, 343 (1947).

ELONGATION HYSTERESIS OF HEVEA AND SYNTHETIC ELASTOMERS *

M. Mooney and S. A. Black

General Laboratories, United States Rubber Co., Passaic, New Jersey

INTRODUCTION

In many of the service conditions where rubber is subjected to repeated cycles of deformation, the operating frequencies lie in the range from 1 to 100 c.p.s. Most hysteresis testing at such frequencies has in the past been carried out with equipment which imposed narrow restrictions on the amplitudes and the mean deformations employed. These restrictions doubtless are the result, partially at least, of the fact that chosen types of deformation have been compression, shear, and flexure, very little work having been done in cycles of elongation except at audio and higher frequencies.

To study hysteresis at high deformations and at fairly high amplitudes, an apparatus, called a *spider hysterometer*, has been developed for measuring hysteresis in cycles of elongation at frequencies from 2 to 60 c.p.s., at temperatures from 0° to 105° C, and over a wide range of mean elongation and amplitude. With this apparatus, a comprehensive survey has been made of the hysteresis of gum stocks of Hevea and of five commercial synthetic elastomers.

BASIC PRINCIPLES OF THE TEST

The principle of the spider hysterometer is not new, having been disclosed in a patent by Shields[1] in 1922; but, to the knowledge of the present authors, no data obtained in the Shields hysterometer have ever been published.

Figure 1 shows the essential parts of the mechanism of the spider hysterometer. Either square-shouldered dumbbell samples or loop samples are attached at A, B, C, etc., on the face of a disk which can be rotated by an external motor. The axis of the disk is horizontal. The other ends of the samples are attached to a freely rotating hub mounted independently of the disk. The hub can be displaced horizontally either parallel to or perpendicular to the disk. If the hub is displaced a distance δ parallel to the disk, the samples undergo a cyclic elongation and contraction from the values $L_1 + \delta$ at position A, to $L_1 - \delta$ at position E, where L_1 is the mean length of the sample in the cycle.

If the samples were perfectly elastic, the horizontal displacement of the hub would not produce any vertical reaction. Any hysteresis in the samples produces a resultant vertical force. This follows because, with directions of rotation and displacement indicated in Figure 1, samples above the center line are undergoing contraction, while those below the center line are undergoing extension. Because of hysteresis, therefore, a sample in position C, for example, exerts less tension than when in position F. The net vertical force on the hub is a measure of the energy loss per cycle in the six samples, due to their hysteresis.

* Reprinted from the *Canadian Journal of Research*, Vol. 28, Section F, No. 4, pages 83–100, April, 1950.

In addition to hysteresis, the mean tension is of interest and also its local variation with extension, or the dynamic differential modulus. The mean tension can be measured by the force required to produce a given displacement of the hub normal to the plane of the disk. The differential modulus is measured by the force required to produce a displacement parallel to the face of the disk;

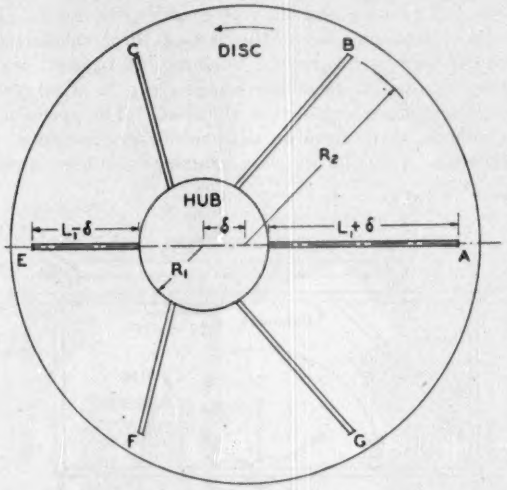


FIG. 1.—Basic design of the spider hysterometer. The large disk is driven. The small disk, or hub, rotates freely on its axis, which is forcibly displaced from the axis of the large disk. Each sample, interconnected between the two disks, executes an elongation cycle of amplitude δ with each revolution of the disk.

but in calculating the modulus, an appreciable correction must be made for mean tension. This correction takes account of the angular asymmetry between such corresponding sample positions as B and C, for example.

MACHINE CONSTRUCTION

The construction of the machine is as shown in Figure 2 and in the photograph, Figure 3. The bearings and drive for the disk are of standard design, and are not shown. The main mechanical feature of the hysterometer is the carriage, $ACEBH$, which supports the hub. The carriage is hung in the half-bearings F and G, in which it is free to slide horizontally as well as rotate. The bearings are lap-fitted, and are lubricated with air, fed continuously under 60 lb. pressure through a pair of small holes in each bearing.

The hub is mounted on a lever, pivoted at point C, which transmits the vertical, or hysteresis, force to the Y balance beam, which rests by a knife edge on the carriage. Changes in the vertical force are balanced by shifting the rider m a distance y to the right or left. The weights on the ends of the Y beam are to increase its moment of inertia, so as to reduce the oscillations of the beam resulting from slight unbalance in the samples. The natural frequency of this beam limits the lowest speed of the disk at which measurements can be made.

To measure the radial force on the hub when displaced parallel to the disk, a weight W_y can be hung from a cord attached to one end or the other of the

carriage, and the deflection of the carriage noted on the scale at *D*. The air bearings are important in reducing the frictional error in this measurement.

The mean tension in the samples is measured by displacing the disk along its axis a distance of approximately ½ inch and determining the moment acting on the *Z* balance beam which will retain the hub in its original position, as determined by a dial gauge in contact with the *Z* balance beam. This measurement is made with the disk turning and the hub radially displaced. To reduce play at the pivots, the vertical member of the vertical force-measuring linkage, *EH*, is locked to the carriage by means of a bushing and tapered pin at point *B*.

The frequency of oscillation of the samples can be fixed by adjusting the speed control mechanism which drives the disk. The speed is measured by means of a tachometer made from an automobile speedometer. The restoring spring was replaced by a weight and cam, which gave a logarithmic speed scale.

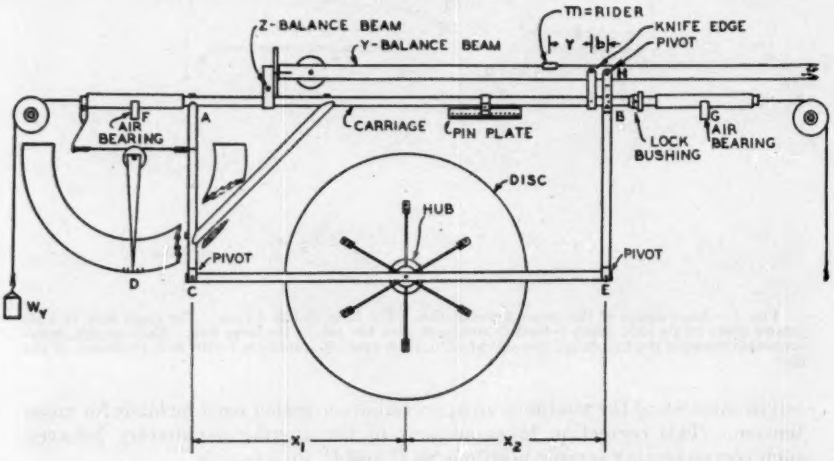


FIG. 2.—Mechanical parts of the spider.

The disk is surrounded by an oven, thermostatically controlled. The lever to which the hub is attached is the only part of the measuring mechanism which extends into the oven. It passes through holes with small but adequate clearance.

The range of the machine with respect to the control of the variables is as follows:

Mean extension—adjustable from 1½ inch to 5¼ inch by means of slotted disk construction which makes possible attachment of the sample hooks at various predetermined positions.

Oscillation amplitude—adjustable from 0 to 2 inches in ¼-inch steps by means of the pin plate, or in smaller steps by means of shims. Alternatively, the amplitude can be controlled by the use of a weight W_y.

Frequency of oscillation—adjustable from 2 to 60 c.p.s.

Temperature—adjustable from 0° to 105° C. Temperatures below room temperature are obtained by forced circulation of air between the disk housing and a dry-ice cooling chamber.

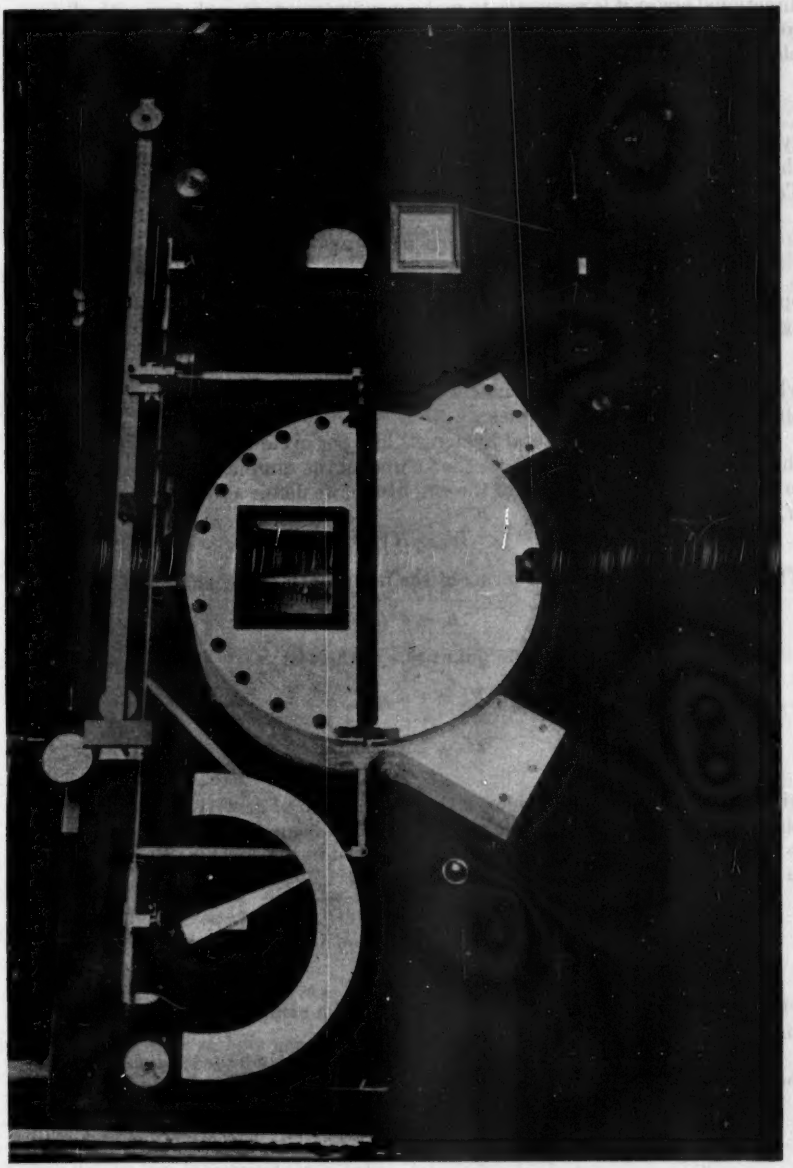


FIG. 3.—Spider hysterometer.

Errors due to friction and windage are directional; and to eliminate these directional errors it is necessary to make measurements in each case with all four combinations of positive and negative rotation and positive and negative displacement δ.

THEORY

All quantities measured in this test are time averages over the period of a cycle, or the time for one revolution of the disk. In the equations involved in the analysis, terms in the second and higher powers of δ/L_1 have been neglected. To this approximation the cycle of elongation is sinusoidal.

ABSOLUTE HYSTERESIS

The vertical force on the hub due to hysteresis constitutes, in effect, a brake opposing the rotation of the disk. The work, W, per revolution per sample against this brake is obviously:

$$W = 2\pi\delta F_v/n \qquad (1)$$

where F_v is the vertical force on the hub, δ is the horizontal hub displacement, and n is the number of samples:

This work is also the total hysteresis loss per cycle per sample. Assuming that the loss is proportional to V, the volume of the sample, and at least roughly proportional to a^2, the square of the amplitude, we define a hysteresis coefficient, H, by the equation.

$$W = HVa^2 \qquad (2)$$

The amplitude is defined in terms of the free length of the sample, L_0. Thus:

$$a = \delta/L_0 \qquad (3)$$

In terms of the measurable quantities in the test:

$$\left.\begin{aligned} F_v &= Cmgy \\ C &= \frac{x_1 + x_2}{bx_1} \end{aligned}\right\} \qquad (4)$$

where m is the mass of the rider, g the acceleration of gravity, and y is the displacement of the rider necessary to keep the Y-beam balanced when the disk is rotated. The apparatus dimensions involved in the constant C are indicated in Figure 2.

From Equations (1) to (4) we obtain:

$$H = \frac{2\pi CL_0mgy}{nA_0\delta} \qquad (5)$$

where A_0, the unstrained cross-sectional area of a sample, has been substituted for V/L_0.

The definition of y, as given, is conceptual rather than operational. As was indicated earlier, the operational definition is:

$$y = \frac{(y_3 + y_4) - (y_1 + y_2)}{4} \qquad (6)$$

where y_3 and y_4 are the two high readings of the balancing rider position, and y_1 and y_2 are the two low readings, the four readings being taken with the four combinations of positive and negative disk rotation and hub displacement.

MEAN TENSION

The mean tension in the samples is measured by displacing the disk axially by a distance z and observing F_z, the axial force on the hub required to hold the hub in its position. Then:

$$F_z = zA_0\sum_1^6 \frac{T_i}{L_i} \tag{7}$$

or with sufficient approximation:

$$F_z = nA_0zT_1/L_1 \tag{8}$$

Here T_i and L_i are, respectively, the tensile force per unit unstrained area and the length of sample i. We may take T_1 as the tensile force at the mean length $L_1 = R_2 - R_1$, where R_2 is the disk radius at the outer ends of the samples, and R_1 is the hub radius at the inner ends of the samples.

DIFFERENTIAL MODULUS

The analysis of the dynamic differential modulus and the associated radial force is somewhat involved. Referring to Figure 4, we see readily that the

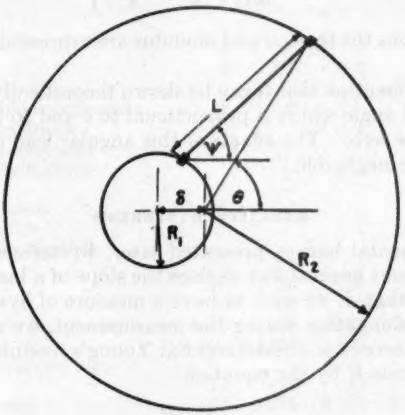


FIG. 4.—Angular and displacement relations. Geometric analysis shows that approximately $\psi = \theta - \frac{\delta}{R_2 - R_1}\sin\theta$, and $L = R_2 - R_1 + \delta\cos\theta$.

mean horizontal radial force is:

$$F_r = \frac{nA_0}{2\pi}\int_0^{2\pi} T\cos\psi d\theta \tag{9}$$

Both ψ and T, the sample tension per unit area, are functions of θ. T is represented adequately by an expression of the form:

$$T = T_1 + \frac{\Delta L}{L_0}(D + h\sin\theta) \tag{10}$$

where ΔL is the increment in length above L_1, D is the mean differential elongation modulus, and h is a constant which is proportional to H. We need not determine the proportionality factor, since h vanishes later from our equations.

It is obvious that ψ differs from θ by only a small amount, and we may let:

$$\psi = \theta + \epsilon \tag{11}$$

and treat ϵ as a small quantity whose higher powers can be neglected. Geometrical considerations then show that, to a first approximation:

$$\left.\begin{aligned} \epsilon &= -\delta \sin \theta/L_1 \\ \Delta L &= \delta \cos \theta \end{aligned}\right\} \tag{12}$$

The integral of Equation (9) can now be evaluated, leading to the result:

$$F_r = \frac{n\delta A_0}{2L_1}\left(T_1 + D\frac{L_1}{L_0}\right) \tag{13}$$

From Equations (8) and (13) we easily obtain:

$$\left.\begin{aligned} T_1 &= \frac{L_1 F_z}{nzA_0} \\ D &= \frac{L_0}{nA_0}\left(\frac{2F_r}{\delta} - \frac{F_z}{z}\right) \end{aligned}\right\} \tag{14}$$

In these equations the tension and modulus are expressed in terms of observable quantities.

It may deserve mention that it can be shown theoretically that the hub leads the disk by a small angle which is proportional to δ and to the vertical, or hysteretic, force on the hub. The effects of this angular lead on the quantities of present interest are negligible.

RELATIVE HYSTERESIS

In the experimental curves presented later, hysteresis varies with mean elongation in the same general way as does the slope of a load-elongation curve. This fact suggests that, if we wish to have a measure of hysteresis which is less dependent on the elongation during the measurement, we should use the ratio of the absolute hysteresis to the differential Young's modulus. We now define the relative hysteresis R by the equation:

$$R = \frac{2H}{D} \tag{15}$$

If a weight is suspended by a rubber cord and is allowed to oscillate in a vertical line about its equilibrium height, then R, by this definition, is the ratio of the energy loss per cycle to the kinetic energy of the weight as it passes through its equilibrium position. $R/2$ is the logarithmic decrement of the oscillation.

RELATIONS WITH OTHER HYSTERESIS UNITS

The coefficient of hysteresis employed in this paper was so chosen as to be as nearly as possible independent of frequency and amplitude. It is different from the coefficients or units employed by other workers in this field, the most commonly employed unit having the dimensions of viscosity. For purposes of comparison the following relationships will be found useful:

$$H = \pi p \eta \tag{16}$$

where $p = 2\pi\nu$, ν is the frequency, and η is the effective "viscosity" of the material at frequency ν.

$$R = 2\pi \tan \lambda = 2\Delta \tag{17}$$

where λ is the loss angle and Δ is the logarithmic decrement.

The analysis of hysteresis in terms of these more conventional parameters is summarized in a recent review by Dillon and Gehman[2].

EXPERIMENTAL RESULTS

The compounds used in these tests are given in Table I, together with some of their physical properties.

TABLE I

COMPOUNDS

	Hevea	GR-S	Hycar	GR-I	Perbunan	Neoprene
Pale crepe	100					
GR-S		100				
Hycar OR-15			100			
Butyl-(GR-I)				100		
Perbunan					100	
Neoprene-GN						100
Zinc oxide	5	5	5	5	5	1
Stearic acid	2	1.5	1	3	1.5	0.5
Zinc stearate				1		
Acetone-diphenylamine condensate	1	2				
Phenyl-beta-naphthylamine			1	0.5		2
Extra-light calcined magnesia						4
Piperdinepentamethylenedithiocarbamate						0.5
2-Mercaptobenzothiazole	1	1.5				
Benzothiazolyl disulfide			1		1	
Tetramethyl thiuram disulfide				1		
Sulfur	2.5	1.5	1	0.5	1.2	
Cure (min.)	35	30	30	30	15	15
At pounds steam	30	50	50	50	50	50
Scott tensile strength (lb. per sq. in.)	4000	188	1500	2300	396	3600
Elongation at break (%)	830	1350	870	1110	620	1090
T_s, second-order transition temperature (° C)	−71	−58	−23	−63	−36	−42
K (torsional hysteresis)	0.038	0.289	0.229	0.182	0.178	0.092

The definition of hysteresis coefficient H in Equation (2) requires, if H is constant, that the energy loss per cycle shall be proportional to the square of the amplitude. A logical first experimental step is to test this relationship. Figure 5 shows H as a function of the amplitude, a, for a GR-I gum stock at 450 per cent mean elongation, 31 c.p.s., room temperature. It is seen that H is not constant; and the curve shows that the loss per cycle increases more slowly than a^2 up to about $a = 30$ per cent, after which the assumed law is approximately obeyed.

While the variation of H and a varies considerably with the stock tested and with the testing conditions, the variation shown in Figure 5 is about as large as any that has been observed.

The maximum mean elongation attainable in the spider hysterometer is limited usually by what the stock will stand without quick failure. Natural rubber is one of the few rubbers which can be tested at over 200 per cent elongation. Figure 6 shows the hysteresis surface for a Hevea gum stock as a function

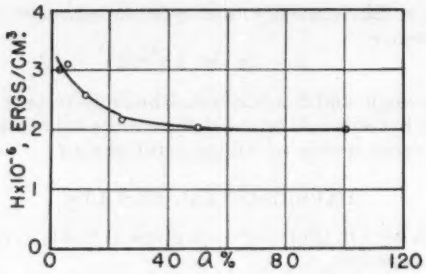


FIG. 5.—Hysteresis as a function of amplitude, a. GR-I gum stock, room temperature, 450% e, 31 c.p.s.

of frequency and mean elongation, at room temperature and 25 per cent amplitude.

There is relatively little variation with frequency, which is in agreement with many other hysteresis tests[2] on Hevea and other elastomers. The variation with elongation, on the other hand, is large. It shows a minimum at 150 to 250 per cent elongation, depending on the frequency.

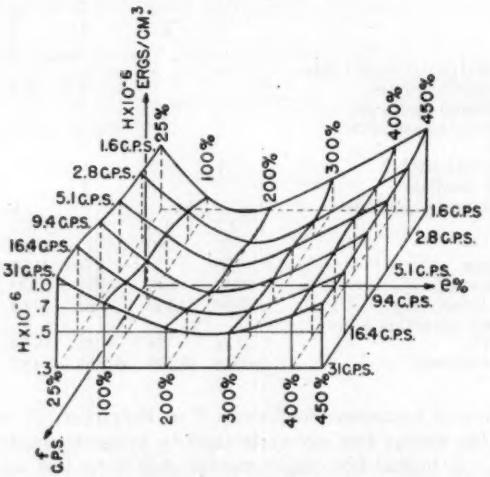


FIG. 6.—Hysteresis surface for Hevea gum stock, as a function of f, frequency, and e, mean elongation. Room temperature, 25% amplitude.

While the frequency effect is very small, there is an interesting variation in this effect with elongation. Thus, at the lowest elongation *viz.*, 25 percent, the hysteresis increases slightly with frequency, whereas at the high elongations, 400 and 450 per cent, hysteresis decreases slightly with frequency.

A comparison between absolute hysteresis, H, and relative hysteresis, R, is shown in Figure 7, which includes also a curve for D, the differential modulus. Although the D and H curves are qualitatively similar, they are far from exactly similar; hence R is not constant, even though it shows much less variation than does H.

The results that have been reported so far were obtained with an early model of the spider hysterometer which lacked temperature control. When the model with temperature control became available, a systematic survey was undertaken of natural rubber and the five synthetic elastomers GR-S, GR-I, Neoprene-GN, Perbunan, and Hycar-OR.

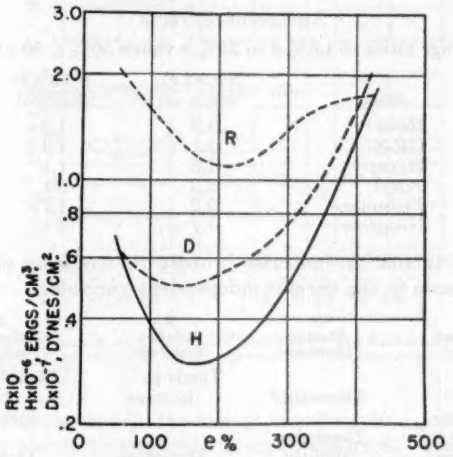


FIG. 7.—Absolute hysteresis, H, differential dynamic modulus, D, and relative hysteresis $R = 2H/D$. Hevea, room temperature, 11 c.p.s., 25% amplitude.

The samples used were all of the T-50, or square-headed dumbbell type, die cut from 0.1-inch sheets, with a shank length of 1.5 inches. For each temperature a fresh group of samples was cut and installed in the machine with a minimum of stretching. The samples were not mechanically preworked. At all times precautions were taken to prevent stretching the samples beyond the elongation at which the test was to take place. As the machine works under fixed strain conditions, this was necessary to reduce as much as possible the errors that would occur in the intercomparison of various stocks which drifted by different amounts during the preworking treatment. After the samples had been installed in the jaws, the jaws were moved out along the face of the disk to the positions corresponding to the smallest mean elongation at which it was desired to work, the carriage was displaced to give the proper amplitude, and the run then made at low, then at high speed. At mean elongations other than the smallest, the samples were measured at two amplitudes, 1.5 and 25 per cent, the smaller amplitude always being used first. Sufficient time at each test condition was allowed to make possible an approach to equilibrium before measurements were made; otherwise it is impossible to balance the machine.

The net result of this testing procedure is that the samples are run on the first cycle of stretch to mean elongation, e, but on a repeated cycle of amplitude a.

Tests were made so far as possible at the following values of the independent variables:

e, mean elongation (%)	16.7	50	100	200
a, amplitude (%)	1.5	25		
f, frequency (c.p.s.)	5	50		
T, temperature (° C)	0	35	70	105

Errors in the measurements at 1.5 per cent amplitude are so large that these data are not presented in detail. Other than the amplitude effects on hysteresis and modulus which are summarized in Table II, no new trend in the behavior of the samples is evident at low amplitude.

TABLE II

AMPLITUDE EFFECTS

Average ratios of 1.5% a to 25% a values 50% e, 50 c.p.s.

Stock	$\frac{H(1.5\%\ a)}{H(25\%\ a)}$	$\frac{D(1.5\%\ a)}{D(25\%\ a)}$
Heva	1.8	1.3
GR-S	1.1	1.4
Hycar	1.5	1.1
Butyl	2.3	2.1
Perbunan	2.2	1.7
Neoprene	1.7	2.1

The following tabulation indicates broadly the response of the dependent variables to increases in the various independent variables.

Independent variable	H, Absolute hysteresis	R, Relative hysteresis	D, Differential modulus
e, Mean elongation	Decreases*	Tends to decrease	Decreases, then increases†
a, Amplitude	Decreases slightly	Decreases	Decreases
f, Frequency	Increases	Increases	Comparatively unaffected
T, Temperature	Decreases	Decreases	Decreases‡

* H varies approximately inversely as $1 + e$, except for crystalline polymers, which exhibit a minimum and subsequent increase in H.
† Variation similar to variation of slope of static stress-strain curve.
‡ Except Hycar and Perbunan at low a and Hevea at low e.

Detailed curves of H versus elongation at 25 per cent amplitude, 5 c.p.s., and at various temperatures are shown in Figure 8. It should be pointed out first that the H-scales are not all the same; and the hysteresis of Hevea is an order of magnitude lower than any of the others. The general trend of the curves is to decrease with elongation, but Hevea and Neoprene at the low temperatures have a minimum between 100 and 200 percent elongation. Temperature effects show considerable variation, both within and between stocks. The absence of a point for GR-I at 0° C, 50 per cent elongation, is due to the fact that this stock is so sluggish at this testing condition that it fails to retract fast enough and buckles instead. Missing points at the higher elongations or temperatures indicate breakages of the samples under these test conditions.

TABLE III

FREQUENCY EFFECT ON HYSTERESIS, AT 35° C, 100% e, 25% a

Stock	H(50 c.p.s.)/H(5 c.p.s.)
Hevea	1.35
GR-S	1.45
GR-I	2.30
Neoprene-GN	1.45
Perbunan	1.20
Hycar OR	1.45

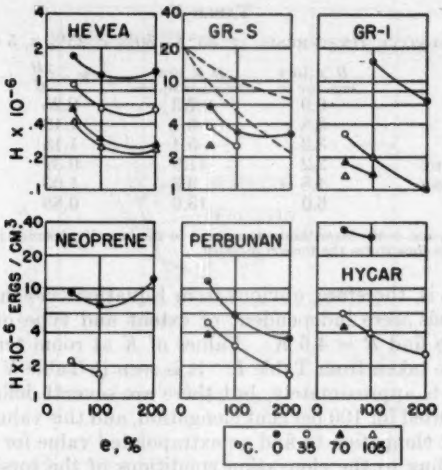


FIG. 8.—Hysteresis of all stocks, at 5 c.p.s., 25% amplitude. The dotted curves in the GR-S section, given for comparison with the experimental curves, represent the functions: upper dotted curve, $20/(1+e)$; ower dotted curve, $20/(1+e)^2$.

The curves of H versus e for the higher frequency 50 c.p.s. are all higher but closely similar to the corresponding curves of Figure 8. Table III shows the magnitude of the hysteresis increase with frequency as observed at 35° C and 100% e.

Table IV gives the dynamic differential moduli observed under the test conditions in Figure 8. The relative hysteresis can be computed by means of Equation (15) from the data of Figure 8 and Table IV. In Table V, R is tabulated for 50% e, 35° C. The torsional hysteresis[3], K, is the damping factor to

TABLE IV

DYNAMIC DIFFERENTIAL MODULUS, $D \times 10^{-8}$, DYNES PER SQ. CM.
Amplitude, 25%; frequency, 5 c.p.s.

		T(° C)			
Stock	e(%)	0	35	70	105
Hevea	50	7.1	7.3	7.8	7.9
	100	5.4	5.2	6.2	
	200	6.9	5.4	5.1	5.4
GR-S	50	9.0	6.4	5.7	
	100	6.5	4.8		
	200	8.2			
GR-I	50		5.37	4.91	3.57
	100	6.36	3.33	3.93	
	200	4.50	2.17		
Neoprene-GN	50	18.6	11.9(?)		
	100	21.2	13.1		
Perbunan	50	15.4	9.3	9.2	
	100	10.8	7.2		
	200	7.5			
Hycar OR	50	21.8	13.6	10.5	
	100	14.0	9.8		

TABLE V

RELATIVE HYSTERESIS AT 35° C, 50% *e*, 25% *a*, 5 C.P.S.

Stock	$H \times 10^{-6}$ ergs per cc.	$D \times 10^{-6}$ dynes per sq. cm.	$R = \frac{2H}{D}$	4.6 *K*
Hevea	0.9	7.3	0.25	0.17
GR-S	3.8	6.4	1.19	1.33
GR-I	3.2	5.4	1.18	0.84
Neoprene	2.2	11.9	0.37	0.42
Perbunan	4.8	9.3	1.03	0.82
Hycar	6.0	13.6	0.88	1.03

K, torsional hysteresis, is the logarithmic decrement to the base 10 observed in a torsion pendulum of which a rubber sample constitutes the torsion member.

the base 10. It is, therefore, obvious from Equation (17) that theoretically, if relative hysteresis were independent of extent and type of deformation, we should expect to find $R = 4.6\ K$. Values of K at room temperature for this comparison were taken from Table I. It is seen in Table V that the expected relationship holds approximately, but there are several definite discrepancies.

If R is calculated for 100 per cent elongation, and this value is combined with R at 50 per cent elongation to find an extrapolated value for 0 per cent elongation, corresponding to the elongation conditions of the torsional test, we still find discrepancies between R and $4.6\ K$.

A comparison of the hysteresis values in Figure 8 with the T_s values in Table I suggests a correlation; the higher the T_s, the higher the hysteresis. In view of this fact, H. M. Smallwood has suggested to the authors that our hysteresis data be plotted against $T - T_s$. This has been done in Figures 9, 10, and 11. It appears that the correlation mentioned does in fact exist, that the

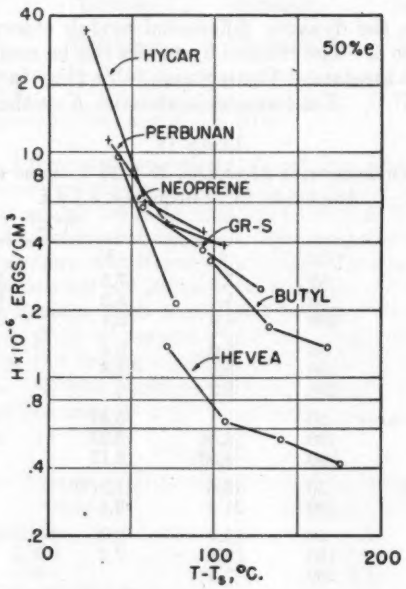


FIG. 9.—Hysteresis of all stocks, at 50% *e*, versus $T - T_s$, T_s being the second-order transition temperature of the respective polymer. Amplitude 25%, frequency 5 c.p.s.

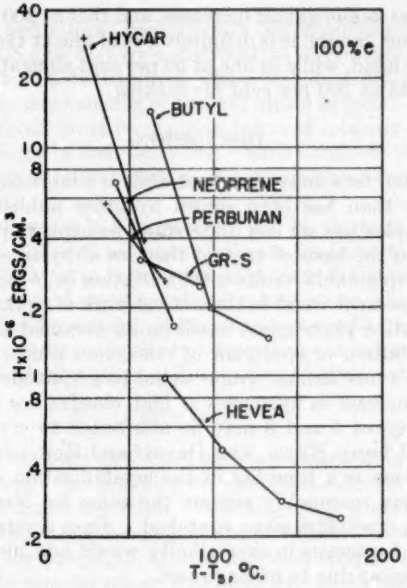


FIG. 10.—Hysteresis of all stocks, at 100% e, versus $T - T_g$, T_g being the second-order transition temperature of the respective polymer. Amplitude 25%, frequency 5 c.p.s.

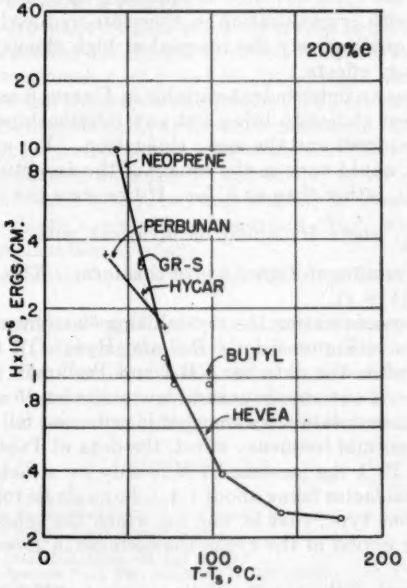


FIG. 11.—Hysteresis of all stocks, at 200% e, versus $T - T_g$, T_g being the second-order transition temperature of the respective polymer. Amplitude 25%, frequency 5 c.p.s.

correlation improves as elongation increases, and that at 200 per cent elongation Hevea is quite in line, though it is definitely out of line at the lower elongations. GR-I, on the other hand, while in line at 50 per cent elongation, is out of line at 100 per cent. Data at 200 per cent are lacking.

DISCUSSION

The data reported here show that hysteresis is a more complex phenomenon in several respects than has been shown by other published measurements. Some of these complexities we can understand or explain qualitatively; others defy explanation on the basis of current theories of hysteresis.

Among the unexplainable results is the variation in H with amplitude shown in Figure 5. The present trend in theoretical work is toward a comprehensive theory of all relaxation phenomena based on an assumed assembly of relaxing units with a distribution or spectrum of relaxation times; but such a theory predicts a hysteresis loss strictly proportional to amplitude squared[4].

The observed increase in hysteresis at high elongations in Hevea and Neoprene shown in Figures 6 and 8 may be attributed to crystallization effects. The experiments of Long, Singer, and Davey[5] and Holt and McPherson[6] have established that there is a time lag in the crystallization of stretched Hevea rubber; and we may reasonably assume the same for Neoprene, which, like Hevea, is known to crystallize when stretched. Since crystallinity has a strong effect on modulus, hysteresis in crystallinity would add mechanical hysteresis to that already present due to other causes.

Since the time lag in crystallization is of the order one second, a cycle of elongation at our high frequencies will be completed before the crystallization at the high end of the cycle has time to approach its equilibrium value. Hysteresis associated with crystallization is, therefore, reduced at high frequency. Thus is explained qualitatively the reversal at high elongations in the sign of the normal frequency effects.

The choice of e as an independent variable in Figures 6 and 8 is arbitrary and perhaps not the best choice to bring out any relationships that might be expected between hysteresis and the mean elongation. For example, it might be felt that hysteresis would vary as the square of the amplitude, but with amplitude defined as δ/L_1 rather than as δ/L_0. If this were the case, we would then have $H = \dfrac{H_1}{(1+e)^2}$, where H_1 would be invariant with e. The lower dotted curve in the GR-S section of Figure 8 is of this form. The upper dotted curve is of the form $H_1/(1+e)$.

Omitting from consideration the crystallizing elastomers Hevea rubber and Neoprene, the data in Figure 8 for GR-S and Hycar-OR fit better the curve $H = H_1/(1+e)$, while the data for GR-I and Perbunan fit better the curve $H = H_1/(1+e)^2$. If any simple general law exists for H as a function of e, at least some of the present data are somewhat in error and fail to indicate the law.

Regarding the normal frequency effect, the data of Table V show that for a frequency ratio of 10/1 the increase in H is only by a factor of 2.3 in one extreme case, the usual factor being about 1.4. For a single relaxation mechanism of the purely viscous type, that is, one for which the relaxation time is small compared with the period of the cycle, the increase in H would be in the ratio 10/1.

By piecing together the results of the present authors and the published results of other workers, it can be shown that absolute hysteresis of rubber in-

creases very slowly and almost linearly with log frequency over at least three decades[7]. To explain this fact by a distribution of relaxation times would require an extremely broad distribution, which would be difficult to account for in terms of molecular mechanisms of the relaxation process. Perhaps the true explanation of hysteresis must be made in terms of relaxing elements which in themselves are nonlinear in their behavior. Such nonlinear elements are postulated in some recent theoretical work on relaxation phenomena in rubbers[8] and in textiles[9] (3, p. 61).

The assemblies of curves in Figures 9, 10, and 11, showing rough correlations between H and $T - T_s$ for all polymers, indicate the important conclusion that hysteresis at all temperatures arises primarily from the same molecular mechanisms or interactions as those which develop brittleness when the temperature is reduced to T_s. The departures, under some test conditions, of Hevea rubber and GR-I from the average curves are larger than the estimated experimental error. Hence, there are also other, still unknown, factors involved in hysteresis.

SUMMARY

A hysteresis test has been developed which measures directly the energy loss per cycle of elongation. Six samples are stretched, like the spokes of a wheel, between a small disk and a large disk. The large disk is motor driven, and the small disk, mounted on a ball-bearing, is displaced eccentrically with respect to the larger disk. In the elongation cycle which each sample undergoes with each revolution, the hysteresis causes an average force on the small disk, which is normal to the eccentric displacement and is proportional to the energy loss per cycle. A lever and balance system makes it possible to measure this force continuously while the machine is running.

Measurements were made on gum stocks of Hevea and five commercial synthetic elastomers. Testing conditions included temperatures, T, of 0°, 35°, 70°, and 105° C; frequencies, f, of 5 and 50 c.p.s.; mean elongations, e, of 50, 100, and 200 per cent and elongation amplitude, A, 25 per cent. Absolute hysteresis, H (loss/cycle-(amplitude)^2), at first decreases with increasing e and then flattens or goes through a minimum. Hysteresis decreases with increasing T. The temperature coefficient between 0° and 35° C is very large for Hycar. Hysteresis usually increases with f, but only slightly in most cases; and Hevea at $e = 400$ per cent shows a reversal of frequency effect, which is presumably associated with crystallization effects.

Under the same conditions, the hysteresis of the synthetics is 10 to 20 times that of Hevea.

When the hysteresis data for all synthetic stocks at various temperatures are plotted against $T - T_s$, T_s being the second-order transition temperature of the respective elastomer, the data lie within a rather narrow band. From this it is concluded that the hysteresis of synthetic elastomers arises from the same molecular forces which cause hardening and embrittlement at and below T_s.

REFERENCES

[1] Shields, U. S. patent 1,595,318 (Aug. 10, 1926).
[2] Dillon and Gehman, *India Rubber World* **115**, 61, 217 (1946); RUBBER CHEM. & TECHNOL. **20**, 827 (1947).
[3] Mooney and Gerke, *India Rubber World* **103**, 29 (1941).
[4] Gross, *J. Applied Physics* **18**, 212 (1947); **19**, 257 (1948).
[5] Long, Singer, and Davey, *Ind. Eng. Chem.* **26**, 543 (1934).
[6] Hott and McPherson, *J. Research Natl. Bur. Standards* **17**, 657 (1936).
[7] Villars, D. S., unpublished survey.
[8] Mooney, Wolstenholme, and Villars, *J. Applied Physics* **15**, 324 (1944).
[9] Eyring and Halsey, in "High Polymer Physics," edited by H. A. Robinson, Remsen Press, Brooklyn, 1948, p. 61

LOW-TEMPERATURE BEHAVIOR OF BUTADIENE–STYRENE COPOLYMERS

EFFECT OF COMPOUNDING VARIABLES *

R. D. JUVE AND J. W. MARSH

THE GOODYEAR TIRE & RUBBER COMPANY, AKRON, OHIO

Synthetic rubbers and natural rubber increase in stiffness at low temperatures and tend to lose their elastic characteristics. This stiffening and hardening phenomenon occurs in varying degrees with various elastomers. Natural rubber and certain synthetic rubbers crystallize during extended exposure at low temperature, whereas other synthetic rubbers such as GR-S remain amorphous[1]. In a general review of the low temperature properties of synthetic rubber, Liska[2] has shown that decreased styrene in butadiene-styrene copolymers improves the flexibility at low temperature.

The low temperature flexibility of vulcanized articles made from any particular rubber or synthetic rubber is influenced by the compounding ingredients admixed with the elastomer. This paper shows the results of some studies of the effect of these compounding ingredients on the low temperature serviceability of butadiene-styrene copolymers. Somewhat similar work on the effect of a large number of plasticizers in GR-S has been conducted at the Rubber Laboratory, Mare Island Naval Shipyard[3], with particular emphasis on compression set at low temperature.

EXPERIMENTAL PROCEDURE

For the evaluation of plasticizers in GR-S, the following compounding recipe was used:

	Parts by weight
GR-S	100.00
EPC black	50.00
Zinc oxide	3.00
Stearic acid	1.00
Sulfur	1.60
Mercaptobenzothiazole	0.62
Diphenylguanidine	0.78
Plasticizer	As shown

In the study of the effect of carbon black particle size on low temperature properties, the recipe which follows was used:

	Parts by weight
Polybutadiene	100.00
Paraflux	6.00
Zinc oxide	3.00
Stearic acid	1.00
Sulfur	2.10
Mercaptobenzothiazole	0.83
Diphenylguanidine	1.04
Carbon black	As shown

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 41, No. 11, pages 2535–2538, November 1949. This paper was presented before the Division of Rubber Chemistry at its semiannual meeting, Detroit, November 8–10, 1948.

The test for low temperature flexibility has been described by Gehman, Woodford, and Wilkinson[4]. The temperatures at which the relative moduli are 2, 5, 10, and 100 times the modulus at 25° C are designated as T_2, T_5, T_{10}, and T_{100}.

Tensile strength and elongation values at 27° C were measured on the Goodyear autographic machine[5], tests at 93° C were made on a standard L-2 Scott tester equipped with a heating jacket. The same machine was used for the tests at −57° C. A standard Scott L-6 tester was placed in a −41° C room for

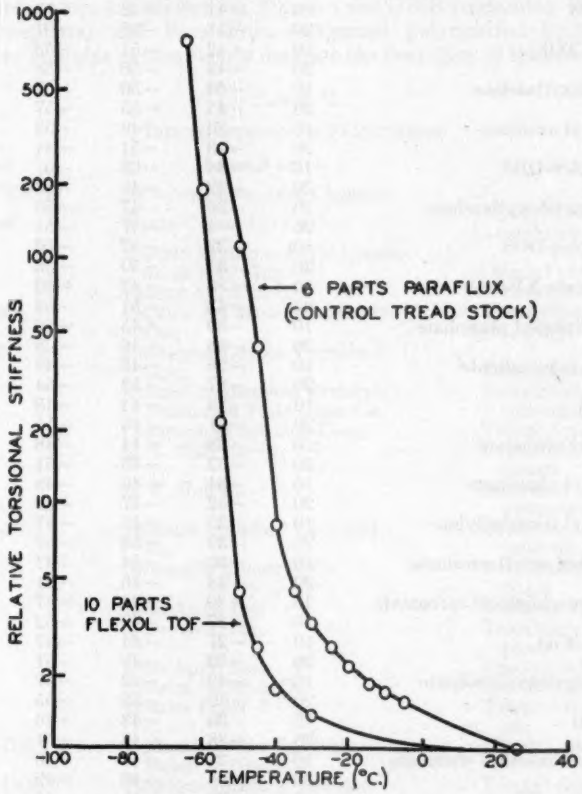


FIG. 1.—Effect of 10 parts of Flexol-TOF on relative torsional modulus of GR-S tread stock at low temperatures.

tests at that temperature. Standard A.S.T.M. dumbbells, 1 × 0.25 inch, were used on the Scott tester. Rebound values were determined on the Goodyear-Healy rebound machine. Hot cut flex-life determinations were made on the Goodyear flexing machine using a rectangular sample $5\frac{1}{8}$ inches long and 0.90 inch wide cut from a standard test sheet. A $\frac{1}{32}$-inch cross wire cut was made at the center. During the flexing, the samples are stretched to 20 per cent elongation. The method for measuring dynamic properties has been described by Gehman, Woodford and Stambaugh[6]. Compression set test was conducted

TABLE I

PLASTICIZERS IN GR-S

Plasticizer	Parts of plasticizer per 100 parts GR-S	Torsion stiffness values, °C			
		T_2	T_5	T_{10}	T_{100}
Butyl Cellosolve pelargonate	10	−38	−51	−56	−61
	20	−53	−60	−63	−76
Di(*n*-hexyl)adipate	10	−37	−50	−45	−62
	20	−48	−58	−62	−69
TP-90B	10	−41	−52	−53	−61
	20	−51	−58	−61	−67
Flexol-TOF	10	−42	−51	−53	−60
	20	−49	−56	−58	−64
Di(*n*-hexyl)azelate	10	−40	−50	−52	−56
	20	−45	−55	−57	−65
Tributyl aconitate	10	−36	−49	−52	−57
	20	−43	−51	−54	−63
Monoplex-DBS	10	−34	−63	−51	−60
	20	−32	−49	−57	−66
Di(2-ethylhexyl)azelate	10	−36	−47	−50	−58
	20	−4	−47	−51	−62
Monoplex-DOS	10	−32	−47	−50	−57
	20	−34	−50	−55	−63
Plasticizer XP-3	10	−33	−47	−50	−55
	20	−38	−51	−54	−60
Octyldiphenyl phosphate	10	−30	−45	−50	−54
	20	−38	−46	−48	−55
Mixed octyl adipate	10	−26	−45	−49	−55
	20	−37	−52	−54	−60
Kapsol	10	−28	−44	−48	−58
	20	−31	−45	−51	−59
Dibutyl phthalate	10	−28	−44	−48	−53
	20	−32	−48	−51	−58
Tributyl phosphate	10	−34	−46	−48	−53
	20	−42	−47	−49	−57
Tributyl tricarballylate	10	−35	−45	−47	−56
	20	−39	−53	−57	−64
Di(mixed octyl) succinate	10	−30	−44	−47	−55
	20	−34	−46	−51	−59
Tetrabutyldiglycol carbamate	10	−30	−43	−47	−55
	20	−37	−49	−52	−60
Flexol-3GO	10	−27	−44	−47	−54
	20	−33	−49	−51	−55
Di(2-ethylhexyl) adipate	10	−19	−42	−47	−55
	20	−42	−52	−55	−62
KP-140	10	−30	−43	−46	−51
	20	−38	−48	−51	−55
Butylbutoxyethyl phthalate	10	−27	−43	−46	−50
	20	−35	−46	−49	−54
Plasticizer-SC	10	−29	−41	−45	−51
	20	−33	−46	−49	−55
Dioctyl phthalate	10	−25	−42	−45	−50
	20	−31	−45	−47	−54
Baker P-4C	10	−25	−40	−44	−51
	20	−30	−45	−48	−54
Para Flux (control tread stock)	6	−18	−39	−42	−50

by a modification of A.S.T.M. D395-47T method B. The percentage compression set was taken as the percentage set remaining after release from 30 per cent compression for 168 hours at −57° C. Volatility is recorded as the weight loss after 48 hours in an air oven at 100° C.

EFFECT OF PLASTICIZERS UPON LOW TEMPERATURE FLEXIBILITY

Twenty-six plasticizers, including those shown in the literature to have very low freezing points, were studied in GR-S. Both 10 and 20 parts of each per 100 parts of GR-S were tested. GR-S was selected for the plasticizer study because it stiffens at a higher temperature than butadiene-styrene copolymers of lower styrene content, thereby allowing a more critical examination of the plasticizing effect. Typical data from which the stiffness values shown on Table I were taken are plotted on Figure 1 for GR-S containing Flexol TOF (trioctylphosphate) and Para Flux (saturated polymerized hydrocarbon). The relative modulus curves clearly describe the flexibility of the stocks.

TABLE II

IDENTIFICATION OF PLASTICIZERS

Plasticizer	Source of sample	Composition
Plasticizer XP-3	Advance Solvents & Chemical	....
Baker's P-4C	Baker Castor Oil Co.	Methyl Cellosolve / Acetyl ricinoleate
	Barrett Division, Allied Chemical & Dye Corp.	Dibutyl phthalate
	Binney & Smith Co.	Dibutyl sebacate
Flexol-3GO	Carbide & Carbon Chemicals Corp.	Triethylene glycol / Di-2-ethyl hexoate
Flexol-TOF	Carbide & Carbon Chemicals Corp.	Trioctyl phosphate
	Columbia Chemical Division, Pittsburgh Plate Glass Co.	Tetrabutyldiglycol carbamate
	Commercial Solvents Corp.	Tributyl phosphate
	C. P. Hall Co.	Butyl Cellosolve pelargonate
Para Flux	C. P. Hall Co.	Saturated polymerized hydrocarbon
Plasticizer-SC	Harwick Standard Chemical Co.	Glycol ester of vegetable oil fat acid
	Monsanto Chemical Co.	Octyldiphenyl phosphate
Kapsol	Ohio-Apex, Inc.	Methoxyethyl oleate
KP-140	Ohio-Apex, Inc.	Tributoxyethyl phosphate
	Ohio-Apex, Inc.	Dioctyl phthalate
	Charles Pfizer & Co.	Tributyl aconitate
	Charles Pfizer & Co.	Tributyl tricarballylate
Monoplex-DBS	Resinous Products Division, Rohm & Haas Co.	Dibutyl sebacate
Monoplex-DOS	Resinous Products Division, Rohm & Haas Co.	Dioctyl sebacate
TP-90B	Thiokol Corp.	High molecular weight polyether

The plasticizers are listed in Table I in order of ascending T_{10} values of the stocks containing 10 parts of plasticizer. It should be observed, however, that in some cases the stocks containing 20 parts plasticizer rate better than the chosen tabulating method would appear to rate them. As an example, tributyl tricarballylate is placed low on the list, but 20 parts of this material resulted in a stock with a T_{10} value at $-57°$ C, which would place it high on the list in comparison to 20 parts of the other plasticizers.

Marked differences in the flexibility of GR-S were caused by the various plasticizers. For example, the substitution of 10 parts of butyl Cellosolve pelargonate for 6 parts of Para Flux lowered the T_{10}, the temperature at which the relative modulus is ten times the room temperature modulus, from $-42°$ to $-56°$ C.

In Table II is given a list of the sources from which plasticizer samples were obtained and a description of the compositions. Plasticizers for which data are given in Table I, but which are not described in Table II, were prepared in the Goodyear Research Laboratory.

In selecting a plasticizer for low temperature applications, it is necessary to consider, in addition to low-temperature flexibility, the volatility and water extraction. Also important are the effects on the processability and the physi-

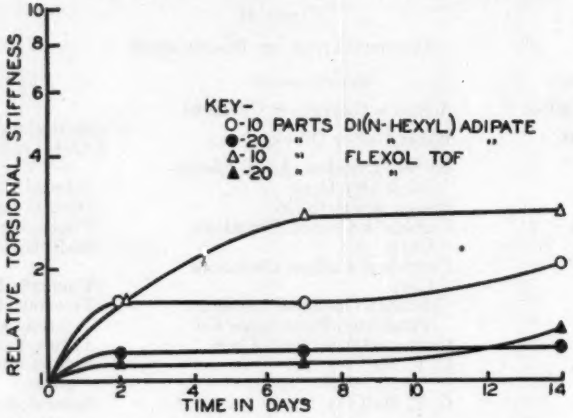


FIG. 2.—Increase in torsional stiffness during long time exposure at $-57°$ C for GR-S containing di(*n*-hexyl) adipate and Flexol-TOF.

cal properties of the rubber. These effects on the final products are not considered herein. For the purpose of this investigation, all of the plasticizers included in this report were miscible with GR-S.

The test results shown in Table I were obtained by rapidly bringing the stocks to test temperature and evaluating them. Some of the best plasticizers from the preliminary screening test were then subjected to long-time exposure tests at low temperature. Figures 2 and 3 describe the increase in relative modulus during 2 weeks' exposure at $-57°$ C. Di(*n*-hexyl) adipate and Flexol-TOF were superior to the others. Ten parts of di(*n*-hexyl)adipate and 10 parts of Flexol-TOF were approximately equivalent to 20 parts of Monoplex-DOS (dioctyl sebacate) and 20 parts of Kapsol (methoxyethyl oleate). The noticeable hardening of GR-S containing 20 parts of di(*n*-hexyl) azelate and 20 parts of Monoplex DBS (dibutyl sebacate) probably can be explained by changes in the solubility of the plasticizers in the rubber.

COMPARISON OF EASY PROCESSING CHANNEL (EPC) AND FINE THERMAL BLACKS IN POLYBUTADIENE

The stiffening effects at low temperature in polybutadiene stocks with 50 parts EPC black, 50 parts of thermatomic P-33 black, and without any black, were compared. With the exception of a slightly higher T_2 temperature, P-33

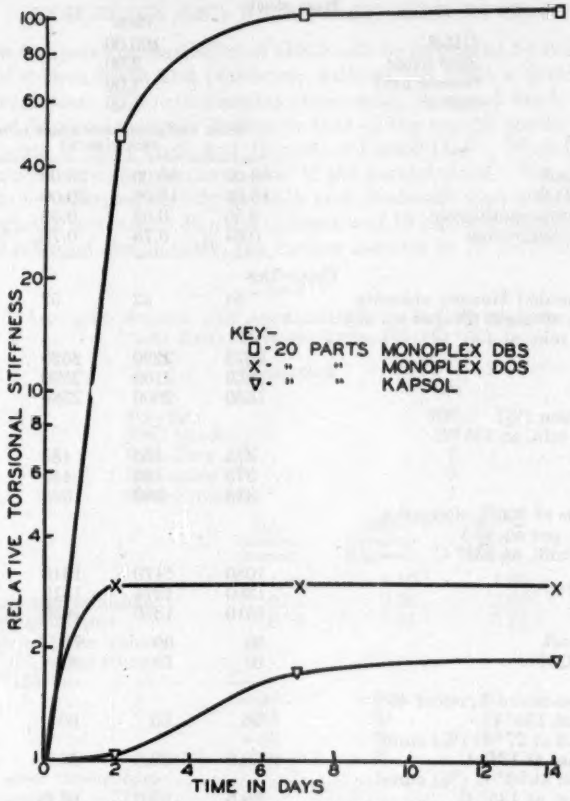


FIG. 3.—Increase in torsional stiffness during long time exposure at −57° C for GR-S containing various plasticizers.

did not seem to change the low-temperature stiffening characteristics exhibited by the gum stock. The presence of 50 parts of EPC black caused the polybutadiene to increase in stiffness somewhat more rapidly. The freezing point of the stock, however, was the same as that of the stock which contained no black. Torsion stiffening data are listed in Table III.

TABLE III

EFFECT OF PARTICLE SIZE OF CARBON BLACK ON FLEXIBILITY OF POLYBUTADIENE AT LOW TEMPERATURES

	Gum stock (no carbon black)	Thermal black P-33	Black EPC
Parts by wt.	..	50	50
Average particle size of carbon black[7] (sq. m. per g.)	..	23	80
Torsion stiffening, ° C (cured 40 min. at 135° C)			
T_2	−60	−51	−44
T_5	−67	−67	−60
T_{10}	−70	−70	−64
T_{100}	−75	−74	−74

TABLE IV—HIGH BLACK–HIGH PLASTICIZER IN GR–S

Base stock

	Parts
GR-S	100.00
Zinc oxide	3.00
Stearic acid	1.00
Sulfur	1.60

	Black and plasticizers added to basic recipe (parts)			
EPC black	50.00	60.00	75.00	75.00
Flexol-TOF	10.00	15.00	20.00	25.00
Mercaptobenzothiazole	0.55	0.62	0.62	0.62
Diphenylguanidine	0.64	0.78	0.78	0.78
Properties				
Compounded Mooney viscosity	51	52	57	47
Tensile, strength (lb. per sq. in.)				
Cure min. at 135° C				
30	2075	2290	2520	2270
40	1850	2100	2590	2420
60	1830	2000	2380	2250
Elongation (%)				
Cure min. at 135° C				
30	475	470	485	470
40	375	420	445	440
60	335	380	395	415
Modulus at 300% elongation (lb. per sq. in.)				
Cure min. at 135° C				
30	1080	1170	1310	1200
40	1300	1275	1510	1375
60	1510	1370	1650	1435
EPC black	50	60	75	75
Flexol-TOF	10	15	20	25
Hardness-Shore A, cured 40 min. at 135° C	56	55	60	57
Rebound at 27° C (%) cured 55 min. at 135° C	58.0	58.0	55.5	55.5
Rebound at 93° C (%) cured 55 min. at 135° C	69.6	69.0	67.9	68.5
Hot cut-strip flex life (min.)				
Cure min. at 135° C				
40	32	40	33	27
80	22	37	31	29
Dynamic resilience, %				
Cure min. at 135° C				
40	29.4	27.8	24.2	25.4
80	31.9	29.0	24.3	25.7
Dynamic modulus (kg. per sq. cm.)				
Cure min. at 135° C				
40	103.0	99.3	113.6	97.3
80	107.8	102.1	116.5	98.3
Internal friction (kp.)				
Cure min. at 135° C				
40	50.4	50.6	62.4	53.2
80	49.6	50.3	65.3	53.5
Torsion stiffening (° C)				
T_2	−25	−34	−35	−40
T_5	−44	−49	−51	−53
T_{10}	−51	−53	−55	−58
T_{100}	−58	−62	−63	−64
% compression set at −57° C after 168 hours' recovery, cured 45 min. at 135° C	84.5	80.0	71.6	66.9
Volatility (% wt. loss) cured 45 min. at 135° C	0.93	0.85	0.96	1.08

HIGH BLACK AND HIGH PLASTICIZER IN GR-S

The low temperature flexibility of GR-S can be improved by increasing the amounts of carbon black and plasticizer without too great a deterioration of physical properties. The compounded stocks with increased black and plasticizer were of Mooney viscosity similar to that of the control stock, which contained 50 parts of EPC black and 10 parts of Flexol-TOF. Moduli at 300 per cent elongation were also similar to that of the control stock. Tensile strength appeared to be increased slightly as black and plasticizer were increased.

Although the increase to 60 parts of black and 15 parts of plasticizer did not change the rebound significantly, the further increase to 75 parts black and 20

TABLE V

ADJUSTED SULFUR AND ACCELERATOR IN POLYBUTADIENE AND BUTADIENE–STYRENE (85/15)

Base stock

	Parts
Polymer	100
EPC black	50
Para Flux	6
Zinc oxide	3
Stearic acid	1

	Polybutadiene (normal)	Polybutadiene (adjusted)	85/15 B/S (normal)	85/15 B/S (adjusted)
Sulfur	1.60	2.10	1.60	1.80
Mercaptobenzothiazole	0.62	0.83	0.62	0.70
Diphenylguanidine	0.78	1.04	0.78	0.88
Torsion stiffness values, (° C), cured 40 min. at 135° C				
T_2	−36	−39	−30	−33
T_5	−58	−60	−53	−51
T_{10}	−68	−69	−59	−57
T_{100}	−79	−77	−70	−69
% set after 168-hr. compression at −57° C, cured 40 min. at 135° C				
After 0.5 hr. recovery	92	91	90	77
After 2 hr. recovery	91	87	84	72
After 24 hr. recovery	90	84	82	65
After 168 hr. recovery	89	81	75	57

to 25 parts plasticizer lowered the rebound at both room temperature and at elevated temperature. Increasing black and plasticizer did not seem to change the flex life. With 60 parts of black and 15 parts of Flexol-TOF, the dynamic characteristics were very similar to those of the control. With 75 parts of black and 20 to 25 parts of Flexol-TOF, the dynamic resilience was lower and the internal friction was somewhat greater.

The stock containing the combination of 60 parts black and 15 parts Flexol-TOF had a 4° C lower freezing point (T_{100}) than the controls. It also had lower compression set at −57° C. Further improvement in low temperature flexibility was caused by increasing the black to 75 parts and plasticizer to 20 to 25 parts. The volatility at 100° C did not seem to be increased significantly by increased black and plasticizer. Physical test data are tabulated in Table IV.

INFLUENCE OF EXTENT OF VULCANIZATION

Polybutadiene and butadiene-styrene (85/15) copolymer, both prepared by emulsion polymerization in a GR-S-type recipe at the Goodyear pilot plant, were compounded in a conventional-type tread recipe at two levels of cure. The two levels used included control stocks with the amount of sulfur and accelerator normally used for GR-S, as well as stocks with sulfur and accelerator increased approximately proportionally to the theoretical increase over GR-S in unsaturation. For the butadiene-styrene (85/15), the sulfur was increased from 1.6 to 1.8 parts, and for polybutadiene it was increased to 2.1 parts per 100 parts by weight of polymer.

The physical test data shown in Table V indicate that the increased sulfur and accelerator had no significant effect on the torsion stiffening results at low temperature. It was found also that when the four stocks described in Table V were exposed for 14 days at −57° C no increase in the relative modulus occurred.

TABLE VI

STRESS–STRAIN CHARACTERISTICS AT LOW TEMPERATURE

	Stock No. 1[a]	Stock No. 2[b]	Stock No. 3[c]	Stock No. 4[d]
	Tested at −57° C			
Tensile (lb. per sq. in.)	3800	3150	3440	4840
Elongation (%)	500	335	225	0
% change from room temp. elongation	+18	−21	−41	−100
	Tested at −41° C			
Tensile (lb. per sq. in.)	2485	3420	...	2670
Elongation (%)	450	460	...	310
% change from room temp. elongation	+6	+4	...	−29
	Tested at room temperature			
Tensile (lb. per sq. in.)	1420	1860	1930	2040
Elongation (%)	425	425	380	435
Freezing point (° C)	−82	−72	−62	−52

[a] Polybutadiene with 6 parts of Flexol-TOF in tread-type recipe.
[b] Butadiene/styrene (85/15) with 6 parts of Flexol-TOF in tread-type recipe.
[c] GR-S with 10 parts of di(*n*-hexyl) adipate in tread-type recipe.
[d] GR-S with 6 parts of Para Flux in tread-type recipe.

The permanent set under static compression at low temperature was investigated using a method similar to that described by Morris, Hollister, and Mallard[8]. The compression set at −57° C was lower for both the polybutadiene and the butadiene-styrene (85/15) copolymer stocks at the higher state of vulcanization. The compression set of polybutadiene was very high at −57° C, even with the improvement caused by increased sulfur and accelerator. No explanation is given for the fact that polybutadiene of excellent low-temperature flexibility should have recovery from static compression inferior to that of a butadiene-styrene (85/15) copolymer of higher freezing point. Since the polybutadiene showed no evidence of stiffening during extended exposure at −57° C, crystallization does not appear to be the explanation.

TENSILE AND ELONGATION CHARACTERISTICS AT LOW TEMPERATURE

Data in Table VI show the tensile strengths and elongations of several stocks at −41° and −57° C. These data show the GR-S, butadiene-styrene (85/15), and polybutadiene to have greater tensile strength at both −41° and −57° C than at room temperature. Although the tensile strength of polybutadiene at room temperature is much lower than that of GR-S, at −41° C, it is almost as good as that of GR-S. There seemed to be some correlation between the freezing point and the percentage change between room temperature elongation and the elongation at low temperature.

ACKNOWLEDGMENT

The authors are grateful to The Goodyear Tire & Rubber Company for permission to publish this work. The cooperation of S. D. Gehman, P. J. Jones, W. D. Wolfe, J. D. D'Ianni, and other members of the Goodyear Research Laboratories in the preparation of experimental polymers and plasticizers and in the determination of physical properties is greatfully acknowledged.

REFERENCES

[1] Sebrell and Dinsmore, *India Rubber World* **103**, 37 (1941); RUBBER CHEM. & TECHNOL. **16**, 857 (1943).
[2] Liska, *Ind. Eng. Chem.* **36**, 44 (1944); RUBBER CHEM. & TECHNOL. **17**, 421 (1944).
[3] United States Navy Department, Bureau of Ships, unpublished report, Washington, D. C., Nov. 3, 1948.
[4] Gehman, Woodford, and Wilkinson, *Ind. Eng. Chem.* **39**, 1108 (1947).
[5] Albertoni, *Ind. Eng. Chem. Anal. Ed.* **3**, 236 (1931); RUBBER CHEM. & TECHNOL. **4**, 591 (1931).
[6] Gehman, Woodford, and Stambaugh, *Ind. Eng. Chem.* **33**, 1032 (1941).
[7] Drogin, "Developments and Status of Carbon Black", Unitel Carbon Co., 1945, pp. 99 and 104.
[8] Morris, Hollister, and Mallard, *India Rubber World* **112**, 455 (1945); RUBBER CHEM. & TECHNOL. **19**, 151 (1946).

LOW-TEMPERATURE STIFFENING OF ELASTOMERS *

S. D. GEHMAN, P. J. JONES, C. S. WILKINSON, JR., AND D. E. WOODFORD

THE GOODYEAR TIRE AND RUBBER COMPANY, AKRON 16, OHIO

In extending the low temperature range for useful applications of elastomers, the phenomena of spontaneous stiffening due to crystallization or other causes must be taken into account. Crystallization, accompanied by progressive stiffening, sometimes occurs over a long period of time. In general, this may be expected in the case of elastomers which have sufficient regularity of molecular structure to show the more familiar phenomenon of crystallization on stretching. Because such elastomers include some of the most useful types of rubber, it is important to understand under what conditions spontaneous crystallization at low temperatures is to be anticipated.

Work reported from the National Bureau of Standards[1], dealing principally with the crystallization and melting of unvulcanized Hevea rubber, furnishes a useful background for the crystallization phenomena with vulcanizates. Observations of the progressive low-temperature stiffening of a class of technical vulcanizates have been published by Gregory, Pockel, and Stiff[2]. Forman[3] investigated the comparative cold hardening of Neoprene, GR-S, and Hevea vulcanizates over a period of time at low temperatures. Conant and Liska[4] observed progressive stiffening with plasticized butadiene-acrylonitrile vulcanizates, which was attributed to low-temperature incompatibility or crystallization of the plasticizer. Forman reported similar effects for plasticized compounds of Neoprene Type FR. Beatty and Davies[5] studied effects of time, temperature, and stress on the behavior of rubber at low temperatures.

The present work comprises a description of what appears to be an improved technique for securing extensive data on the progressive stiffening of elastomers, a survey of the effects of temperature and other significant variables on the crystallization of typical vulcanizates of technically important elastomers, and a discussion of the results to reach an understanding of their significance in terms of general principles applicable to crystallization and the molecular structure of elastomers.

EXPERIMENTAL METHOD

A method of measuring the torsional stiffness of rubber samples previously described[6] has been adapted for securing data on the stiffening from prolonged exposures to low temperature. Figure 1 is a photograph of the assembled apparatus. The test-strips were mounted in supplementary racks, as shown in Figure 2. Ten of these racks were available for the investigation, so fifty samples could be run concurrently.

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 42, No. 3, pages 475–482, March 1950. This paper was presented before the Division of Rubber Chemistry at the 116th meeting of the American Chemical Society, Atlantic City, N. J.

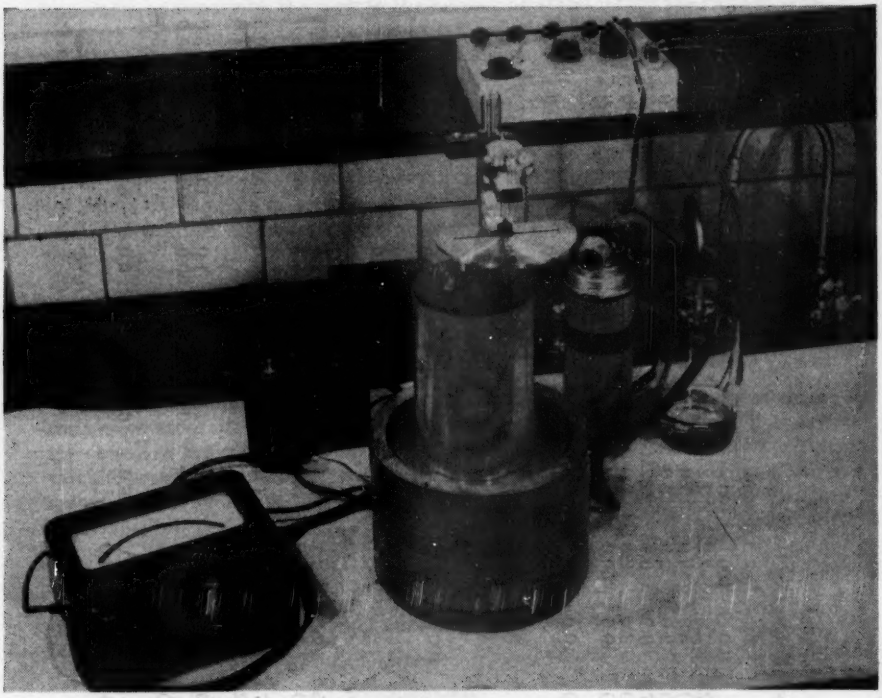


FIG. 1.—Torsional flexibility apparatus.

The torsional stiffness of each test-piece was measured at room temperature and at the storage temperature. The racks were then stored in constant temperature cold boxes or cold rooms at the desired temperatures. It was found advantageous to invert glass beakers over the racks to minimize the chances of any temperature variation of the samples due to opening a cold box during the course of the tests. The racks were removed at suitable intervals and the test-pieces were measured, without changing their temperature, by transferring the rack to be measured into the appropriately precooled insulated cylinder of the

FIG. 2.—Test racks.

TABLE I

COMPOUND FORMULAS USED

Materials	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Smoked sheet rubber	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Sulfur	3.0	3.0	3.0	3.0	2.25	2.25	2.25	2.25	2.25	2.25	2.25	2.25	2.25	2.25
Zinc oxide	3.0	3.0	3.0	3.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	3.0	3.0	3.0	3.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Captax	0.8	0.8	0.8	0.8	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Phenyl-2-naphthylamine	1.0	1.0	1.0	1.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
EPC black	50.0	30.0	15.0	..	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0
Paraflux	6.0	6.0	6.0	6.0	..	..	..	..	..	..	..	..	..	..
Dioctyl sebacate	..	..	..	..	3.0	10.0	20.0	30.0	50.0	..	..	..	..	..
Trioctyl phosphate	..	..	..	..	..	..	..	..	..	3.0	10.0	20.0	30.0	50.0

	15	16	17	18	19	20	21	22	23	24	25	26	27	28
85/15 B/S (5° C)	100	100	..	..	..	..	..	..	..	..	..	..	..	..
85/15 B/S (50° C)	..	..	100	100	..	..	..	..	..	..	..	..	..	..
Polybutadiene (50° C)	..	..	..	..	100	..	..	..	..	..	..	..	..	..
GR-S-10	..	..	..	..	..	100	..	..	..	..	..	..	..	..
Polybutadiene (5° C)	..	..	..	..	..	..	100	..	..	..	..	..	..	..
GR-S	..	..	..	..	..	..	..	..	25.0	50.0	75.0	100	..	..
Smoked sheet rubber	..	..	..	..	..	..	..	100	75.0	50.0	25.0	..	..	..
Neoprene Type GN	..	..	..	..	..	..	..	..	..	..	..	..	100	..
Butyl rubber	..	..	..	..	..	..	..	..	..	..	..	..	..	100
Sulfur	2.5	2.5	2.5	2.5	2.5	2.5	2.1	2.5	2.5	2.5	2.5	2.5	..	2.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	3.0	5.0	5.0	5.0	5.0	5.0	5.0	3.0
Magnesia	..	..	..	..	..	..	..	..	..	..	..	..	4.0	..
Captax	0.75	1.0	0.75	1.00	0.75	0.75	0.55	1.0	1.0	1.0	1.0	1.0	..	0.5
Tuads	0.25	..	0.25	..	0.25	0.25	..	..	..	..	..	..	..	1.0
Diphenylguanidine	..	..	..	..	..	..	0.64	..	..	..	..	..	..	..
Stearic acid	1.0	1.0	1.0	1.0	1.0	1.0	2.0	1.0	1.0	1.0	1.0	1.0	1.0	3.0
EPC black	..	..	..	..	..	..	50.0	50.0	50.0	50.0	50.0	50.0	..	45.0
Gastex black	40.0	40.0	40.0	40.0	40.0	40.0	..	..	..	..	..	..	..	..
Cumar-CX	..	..	..	..	..	..	..	..	..	..	..	..	5.0	..
Paraflux	..	..	..	..	..	..	..	6.0	6.0	6.0	6.0	6.0	..	..
Trioctyl phosphate	..	..	..	..	..	..	6.0	..	..	..	..	..	..	..
Rubber process oil	..	..	..	..	..	..	..	..	..	..	..	..	..	3

apparatus and carrying the rack to the measuring stand where the storage temperature was maintained. After measurement, the rack was removed from the insulated cylinder in the cold box if it was desired to continue the test.

In the presentation of the results, the ratio of the torsional modulus measured at various time intervals to the original modulus at the storage temperature is plotted on a logarithmic scale against time. Thus the plots show directly the relative change in modulus brought about by the storage at low temperature. The relative modulus at room temperature is represented on the graphs by points on the axis of ordinates, so that the overall relative stiffening from room temperature to the storage temperature at any subsequent time also can be obtained.

COMPOUNDS USED

The compound formulas which were used are given in Table I.

COMPARISON OF VOLUME AND STIFFNESS CHANGES

Because the stiffness changes observed in this work over extended periods of time were attributed primarily to crystallization, it was desirable to compare the course of the stiffening with a more direct measure of crystallization. For this purpose, simultaneously with one of the stiffness tests in a cold room, observations were made of the volume changes of pieces of the same compound in a mercury-filled dilatometer. The results of this comparison are shown in Figure 3.

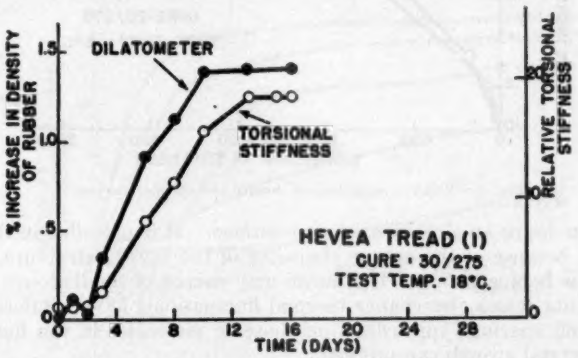


FIG. 3.—Correlation of density and stiffness changes.

The similar shape of the two curves indicates a close correlation between the increase in density of the rubber and the stiffening. The plot in Figure 4 shows, however, that the percentage increase in stiffness far exceeds the percentage increase in density. The stiffness is evidently very sensitive to crystallization. The structural picture which should be kept in mind to understand this result is that the density increase is concentrated in small crystallites, whereas only the average density is deduced from a dilatometer measurement. The crystallites stiffen the rubber, not only because they are relatively stiff themselves, but because they introduce fixed points in the molecular network structure, thus reducing the flexibility of the remaining amorphous material. It is interesting to note from the curves in Figure 4 that the effectiveness of the crystallites on a percentage basis for increasing the stiffness was about the same for both gum and tread stocks.

CHARACTER OF CRYSTALLIZATION PROCESS IN ELASTOMERS

The fundamental thermodynamic theory of a phase change, the direction of which is controlled by the free energy, must, of course, apply to the spontaneous crystallization of elastomers. The rate of transformation is not given by simple thermodynamic theory, so theories of the rate of crystallization become more elaborate and include such concepts as transition through an activated state.

The problem in the development of the theory of crystallization of elastomers lies in the identification and formulation of the role which the various structural features play in the process. There is reason to suppose that, as in other media, the crystallization process involves the formation of crystal nuclei and subsequent growth from these centers[7]. The nucleation is called homogeneous if it occurs in the material itself, and heterogeneous if it occurs on

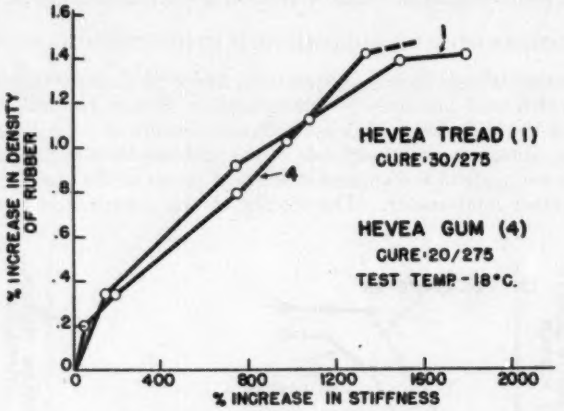


FIG. 4.—Relative magnitude of density and stiffness changes.

foreign particles or an already existing interface. It is plausible in the case of elastomers, because of the unique character of the crystal structure, that the nucleation is homogeneous. The nuclei may consist of small groups of molecular segments which, by chance thermal fluctuations, have assumed relative positions and spacings approximating those of molecules in the final crystal lattice so crystal growth can proceed.

The induction period before crystallization starts, illustrated by the curves in Figure 3, represents the time required for the formation of nuclei. In a recent development of phase transformation theory[8], it is shown that the nuclei must exceed a critical size before continuous growth can occur. This is a consequence of the free energy change in the vicinity, which includes terms due to the interfacial free energy, the bulk free energy difference between the phases, and the strain energy. In the case of elastomers, the growth from a single nucleus is limited, and only small crystallites occur, even when the number of crystallites is low. The limitation to the size of the crystallites probably arises from entanglements which are encountered in the network structure as the crystal lattice is propagated and which offer insurmountable barriers to the rotation or movement of additional molecular segments into the lattice. The average length of the crystallites might provide a measure of the average distance between such structural features as cross-linkages, branches, or hard en-

tanglements. The rapid increase in the degree of crystallinity after the induction period, such as is shown by the curves in Figure 3, implies that new nuclei are being formed at a rapid rate. This process is retarded again as the transformation becomes more complete.

The curves in Figure 5 show the stiffening or crystallization for a series of cures of a Hevea tread stock at −35° and −57° C, respectively. As others have observed[9], the process is dominated by the state of cure as indicated by the combined sulfur values shown. The percentage of combined sulfur is calcu-

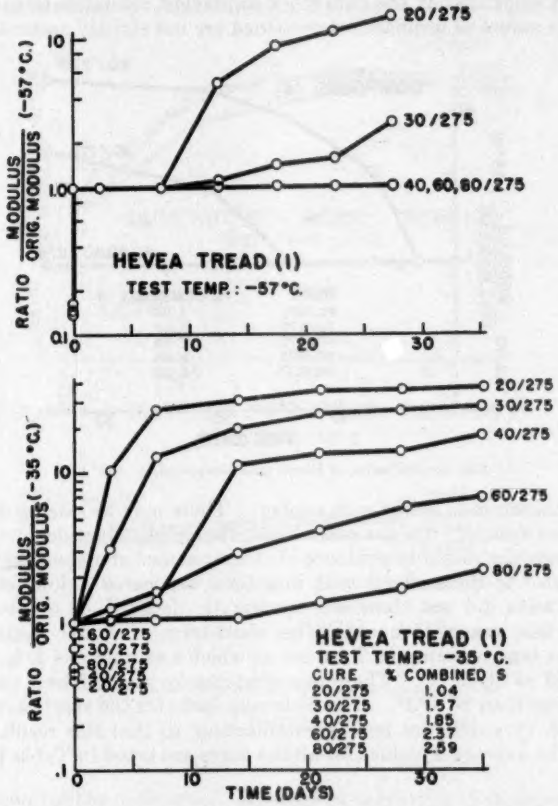


Fig. 5.—Stiffening of Hevea tread compound.

lated on the amount of rubber in the compound. The cross-linkages or other chemical irregularities introduced by the combined sulfur interfere with the crystallization to such an extent that 2.5 per cent of combined sulfur appears to be sufficient practically to forestall spontaneous crystallization in natural rubber. This may be readily understood when the sulfur combination is viewed as bringing about the formation of a relatively immobile molecular network structure with fixed points which cannot be accommodated in a crystal lattice.

Figure 6 shows the stiffening observed for a Hevea gum stock stored at −35° C. Only the two lower cures crystallized. This was also the case when

the samples were stored at −29° C. At −57° C there was no evidence of crystallization for any of the cures.

In comparing the crystallizing tendencies of the gum and tread stock, it appears that these tendencies were much more pronounced in the latter. Most of this effect is due to the difference in the combined sulfur values for the same time of cure. But the 60-minute cure of the tread stock with 2.37 per cent combined sulfur definitely crystallized, whereas the 40-minute cure of the gum stock with 2.38 per cent did not. Either more combined sulfur was required for the rubber in the tread stock than in the gum stock to prevent crystallization, or the combined sulfur values as ordinarily determined are not strictly accurate in reflect-

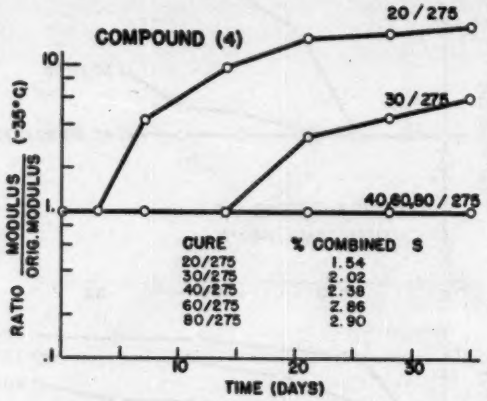


Fig. 6.—Stiffening of Hevea gum compound at −35° C.

ing the combination of sulfur with rubber. There may be side reactions in the vulcanization system. On the other hand, the increased tendency of the tread stock to crystallize might be evidence of at least some heterogeneous nucleation.

In contrast to these effects with long-term exposures to low temperatures, short-term tests did not show any systematic dependence on the combined sulfur for this range of cures. The short-term torsional flexibility test[10] provided the temperatures, or T values, at which a sample was 2, 5, 10, and 100 times as stiff as at 25° C. These temperatures for the different cures did not differ by more than 2° or 3°. The molecular basis for the short-term stiffening is, of course, very different from crystallization, so that this result is not surprising. The average T values for all the cures are listed in Table II.

Table II

Average T Values for Hevea Tread and Gum Stocks

	Compound 1 tread (° C)	Compound 4 gum (° C)
T_2	−38	−58
T_5	−51	−61
T_{10}	−55	−62
T_{100}	−64	−67

The higher T values for the tread stock imply some significant alteration in either the secondary valence forces or the segmental molecular mobility, due to the introduction of carbon black into the compound. The carbon black does

not interefere with the molecular motion necessary for spontaneous crystallization; hence the mobility of the molecular segments does not seem to be seriously impaired. The increased sensitivity of the secondary valence forces to temperature when the carbon black is present is rather difficult to understand. It is fairly certain that the carbon black particles are attached to the rubber molecules by secondary valence forces. Thus some of the secondary valence forces between rubber molecules in the gum stock are replaced in the tread stock by secondary valence forces between carbon and rubber molecules. It is possible that these forces have a greater temperature dependence than the mutual

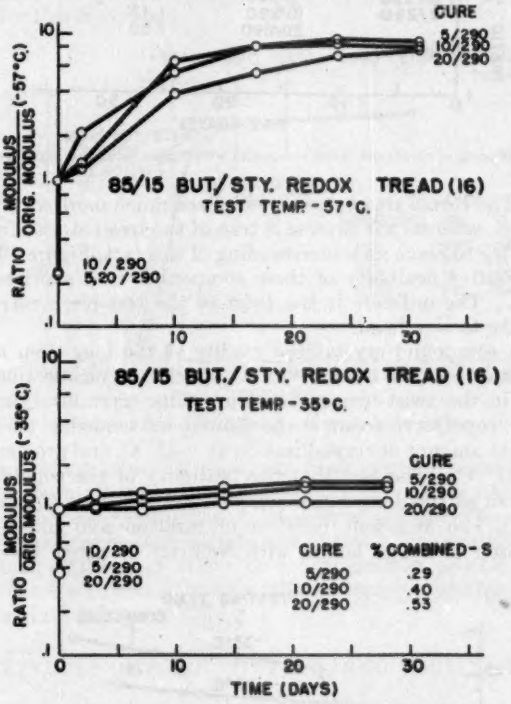


FIG. 7.—Stiffening of copolymer tread compound.

forces between rubber molecules. Another possibility is that changes in temperature set up a system of microstresses in the tread stock, due to the difference between the thermal coefficients of expansion of carbon black and rubber. These internal stresses might lead to a greater temperature sensitivity for the tread stock compared to the gum stock.

Figures 7 and 8 show stiffening curves for tread stocks of an 85–15 butadiene-styrene polymer, the polymerization having been carried out at 5° C. In comparing the curves at −57° C, it is at once evident that the higher state of cure produced by Formula 15 when compared to Formula 16 results in less crystallization.

The crystallizing tendencies of Hevea and the copolymer at −35° C, compared to −57° C, show a marked contrast, which is brought out by the curves

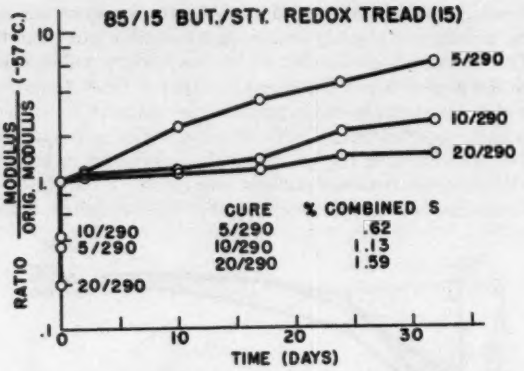


FIG. 8.—Stiffening of copolymer tread compound with higher combined sulfur at −57° C.

in Figure 9. The Hevea tread stock crystallized much more readily at −35° C than at −57° C, whereas the reverse is true of the tread stock of the redox copolymer. To try to reach an understanding of this fact, Figure 10 gives curves showing the relative flexibility of these compounds in a short-term torsional flexibility test. The ordinate is the twist of the test-piece corresponding to 180° twist of the torsion head.

The Hevea compound crystallized readily at the long-term test temperatures of −18° and −35° C, but at −57° C, which is a considerable distance below the bend in the twist-temperature curve, its crystallization was greatly reduced. The copolymer tread stock showed no tendency to crystallize at −18° C, a slight amount of crystallization at −35° C, and pronounced crystallization at −57° C. The fact that the flexibility of the copolymer was but slightly impaired at this lowest test temperature indicates that the molecules themselves still had sufficient freedom of rotation and movement for the segments to enter a crystal lattice with facility. In other words, the closer

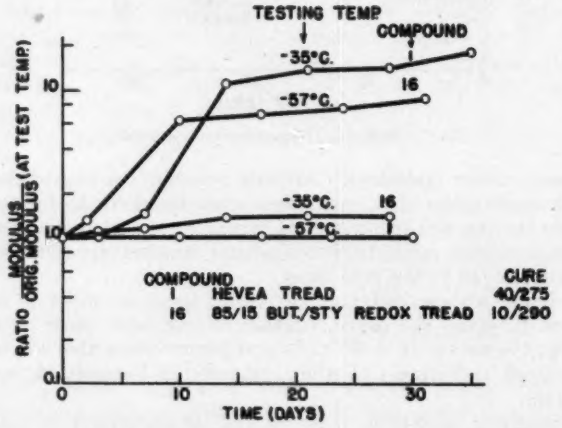


FIG. 9.—Contrast in effect of temperature on stiffening of Hevea and copolymer tread compounds.

approach of the molecules at the lower temperature resulted in an effective increase in the molecular forces favoring crystallization, without unduly hindering the rotations and movements required for the molecules to adjust themselves in the lattice. For the Hevea compound, on the other hand, considerable stiffening occurred at −57° C without crystallization, indicating that the freedom of rotation and movement of the molecules were greatly restricted at this temperature. Consequently, crystallization was hindered, and an optimum temperature range for crystallization was observed. This was only broadly determined in this work, but appears to lie between −25° and −45° C for this compound.

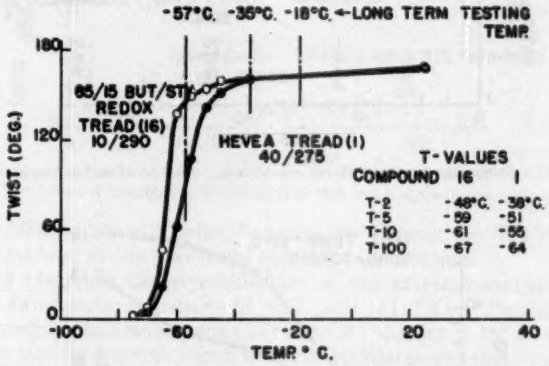


FIG. 10.—Torsional flexibility of Hevea and copolymer tread compounds.

An optimum temperature for the crystallization of unvulcanized Hevea was well defined by the work at the Bureau of Standards[11]. It is interesting to note that a general thermodynamic theory of nucleation[8] predicts a maximum in the curve representing the steady-state rate of thermal nucleation when plotted against the temperature. A study of the nucleation process in elastomers might show that the existence of an optimum temperature for crystallization can be explained on this basis.

EFFECTS OF SOME COMPOUNDING VARIABLES

From the results already given, it is evident that any compounding variables which affect the combination of sulfur have an influence on spontaneous crystallization. It is always necessary to take into account possible variations in combined sulfur in assessing the effect of an ingredient on spontaneous crystallization. Thus the curves in Figure 11 seem to show a dependence of the crystallization on carbon black loading, but actually any effect of the carbon black in this test was dominated by the variations in combined sulfur which occurred.

Plasticizers also may cause variations in combined sulfur when other ingredients in a formula remain the same and the curing cycle is the same. In addition, there is the possible complication of low-temperature incompatibility resulting in a gradual stiffening. Figure 12 gives curves illustrating the effect on spontaneous stiffening of varying the amount of trioctyl phosphate in a Hevea tread compound. There was a relatively small variation in the com-

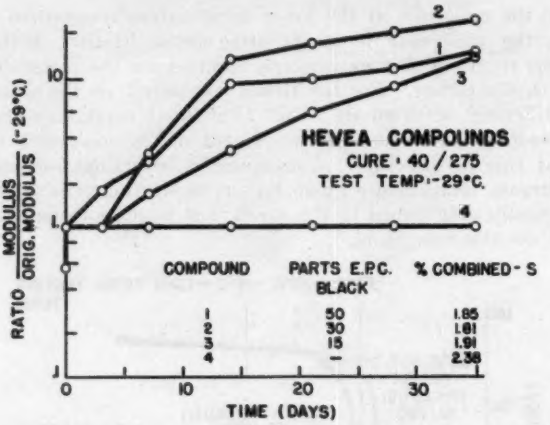


FIG. 11.—Stiffening of series of Hevea compounds. Amount of carbon black varied.

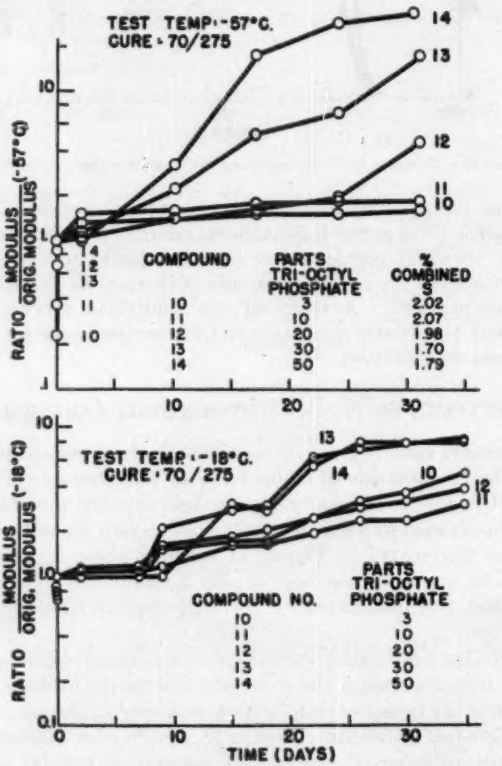


FIG. 12.—Stiffening of series of Hevea tread compounds. Amount of plasticizer varied.

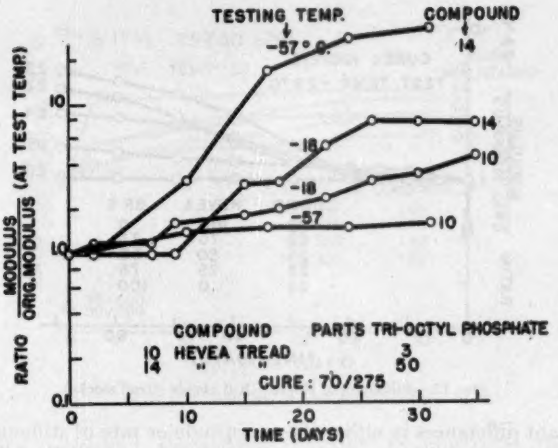


FIG. 13.—Effect of temperature of stiffening of high and low plasticized compounds.

bined sulfur, not sufficiently large, however, to obscure the fact that crystallization was favored as the plasticizer content was increased.

Figure 13 compares the crystallization of the extreme compounds in the series at the two test temperatures of −57° and −18° C. The highly plasticized compound crystallizes more readily at −57° than at −18° C, whereas the reverse is the case for the compound with low plasticizer content. Study of the short-term torsional flexibility curves given in Figure 14 leads to the same explanation of this temperature dependence of spontaneous crystallization that was advanced to explain the results illustrated in Figures 9 and 10. If the plasticizer maintains the flexibility of the compound at lower temperatures, it may be expected that the optimum temperature range for spontaneous crystallization will be displaced to lower temperatures when compared to that for the unplasticized compound.

Tests were made extending over 70 days at −40° C with the series of Compounds 5 to 9, inclusive, which contained varying amounts of dioctyl sebacate.

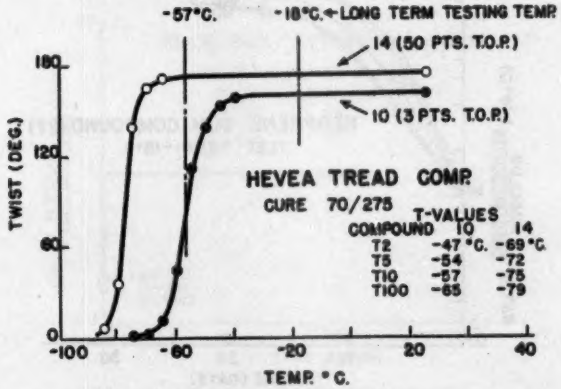


FIG. 14.—Torsional flexibility of high and low plasticized compounds.

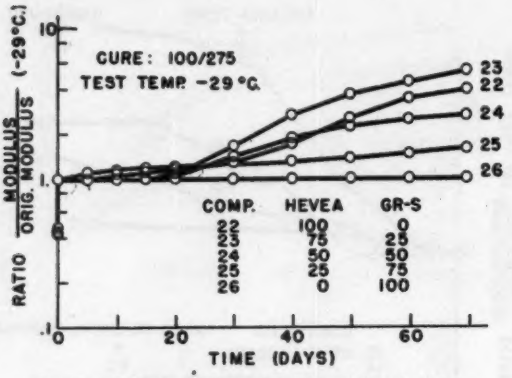


FIG. 15.—Stiffening of Hevea-GR-S blends (tread stocks).

No significant differences in either the magnitude or rate of stiffening occurred in the series, except in the case of Compound 9, for which the stiffening was greatly reduced and retarded.

The curves in Figure 15 show the spontaneous stiffening of blends of GR-S and Hevea. The admixture of GR-S did not seem to delay the crystallization of the Hevea which was present, but tended to prevent the stiffening from proceeding as far as it otherwise would. The crystallization of Hevea in such blends undoubtedly depends on the proportion of the sulfur with which it combines—that is, its rate of cure in the blend. This may lead to rather complicated effects in the study of the spontaneous crystallization of such blends.

SPONTANEOUS CRYSTALLIZATION OF ELASTOMERS

The only elastomers that may be expected to undergo spontaneous crystallization are those that also develop crystallinity on stretching. Figures 16 and 17, for instance, show progressive stiffening for a Neoprene Type GN and a

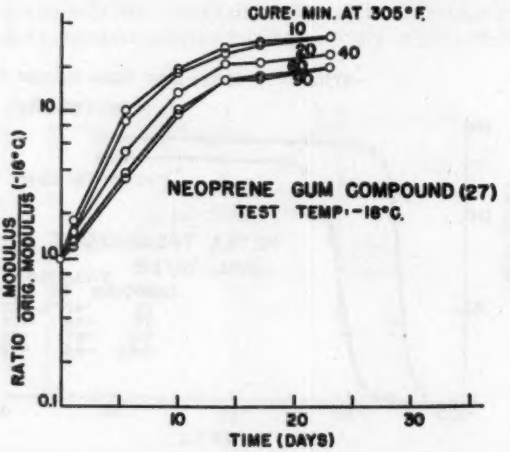


FIG. 16.—Stiffening of Neoprene type GN compound.

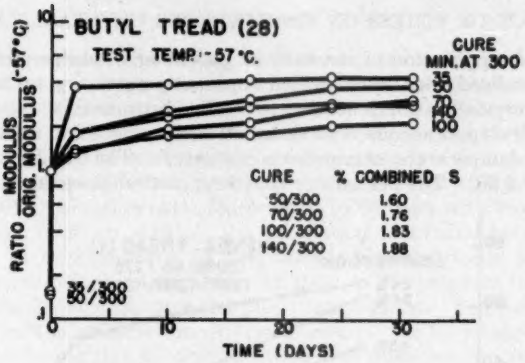


FIG. 17.—Stiffening of Butyl compound.

Butyl rubber compound, respectively. Figure 18 illustrates the complete absence of the phenomenon for a tread stock from an 85–15 copolymer of butadiene and styrene polymerized at 50° C. This can be compared with the results given in Figure 7 for a similar copolymer prepared in a redox polymerization formula at 5° C. It is apparent that the low-temperature copolymer possesses sufficient regularity of structure to make crystallization possible. At the higher polymerization temperature, the most important irregularities are probably due to a heterogeneous *cis* and *trans* chain structure and chain branching. No evidence of spontaneous crystallization was observed in any of the tests with compounds in which the copolymer was prepared at 50° C—*i.e.*, Compounds 17, 18, 20, and 26. Polybutadiene compounds 19 and 21 both showed a slight tendency toward spontaneous crystallization, the stiffness increasing by a factor of about 2 in a 30-day test at −57° C; the cure was, respectively, 10 minutes at 290° F and 40 minutes at 275° F. Improved physical properties, especially tensile strength and flex life, are generally associated with regularity of structure as made evident by crystallinity; but the tendency toward spontaneous crystallization is also enhanced.

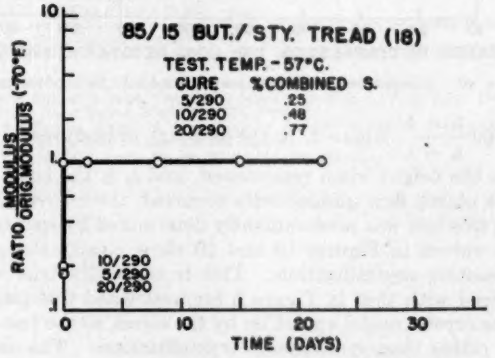


FIG. 18.—Stiffening of copolymer tread compound.

EFFECT OF STRESS ON SPONTANEOUS CRYSTALLIZATION

In general, application of stress to an elastomer produces molecular alignments and localized orientations which apparently act as crystal nuclei, so that spontaneous crystallization is accelerated. To illustrate this, data on the effect of stress on the spontaneous crystallization of Compound 1 were obtained by using a low temperature compression set test[12]. The results are shown in Figures 19 and 20. The percentage recovery, plotted as ordinate in Figure 19,

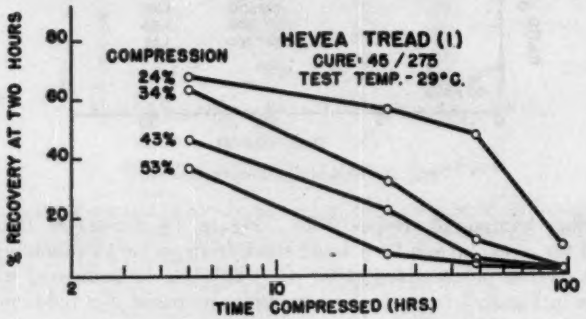


FIG. 19.—Effect of duration and amount of compression on recovery.

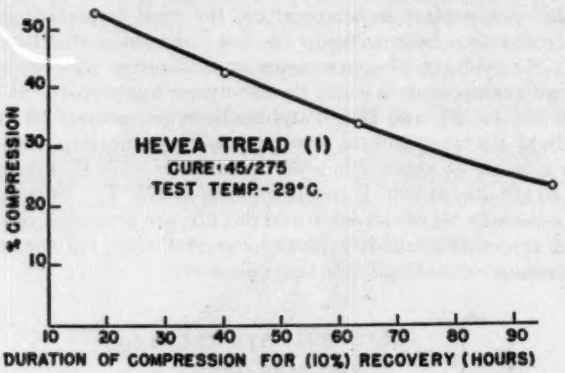


FIG. 20.—Duration and amount of compression for 10 per cent recovery.

is defined as $100\,\frac{t_z - t_s}{t_o - t_s}$, where t_o is the original uncompressed height of the test-piece, t_s is the height when compressed, and t_z is the height after release. Although some plastic flow undoubtedly occurred, the recovery, or rather lack of recovery, in this test was predominantly determined by spontaneous crystallization. The curves in Figures 19 and 20 show clearly the effectiveness of stress for promoting crystallization. This is especially true when the time scale is compared with that in Figure 5 for unstressed test-pieces. In a test under stress the crystal nuclei are set up by the stress, so the test becomes a test of progressive rather than spontaneous crystallization. The usually desirable property of readily forming crystallites under stress can affect the results in the same way as undesirable spontaneous crystallization.

SUMMARY

The generally observed stiffening of elastomers at low temperatures may be supplemented by the occurrence of crystallization if the elastomers have sufficient regularity of molecular structure and other conditions are favorable. To study these effects, observations of the progressive stiffenings of elastomer compounds at low temperatures were made by measurements of the relative torsional modulus of test strips mounted in racks which were stored at low temperature. The periods of observation extended over 30 to 60 days with temperatures in the range from −59° to −18° C. A correlation was found between density changes due to crystallization as determined dilatometrically and torsional stiffness changes. Factors studied in addition to temperature included compounding variables such as cure and plasticizer content. Some data were obtained to show the acceleration of crystallization due to compressive stress. Progressive stiffening due to crystallization was observed for vulcanizates of Hevea, Neoprene Type GN, and Butyl rubber, as well as for an 85–15 butadiene-styrene redox-type copolymer. The results were interpreted in accordance with concepts of crystal nucleation and growth with necessary modifications due to the molecular structure of elastomers. Although the phenomenon of spontaneous crystallization of elastomers was found to be complicated by many factors, a useful degree of generality appears in some of the results.

ACKNOWLEDGMENT

The authors wish to express their thanks to the Goodyear Tire and Rubber Company and to H. J. Osterhof for permission to publish this work, to G. H. Gates, R. D. Juve, and Edward Cousins for formulating the compounds used, and to H. E. Rutledge for the combined sulfur determinations. This investigation was carried out under the sponsorship of the Office of Rubber Reserve Reconstruction Finance Corporation, in connection with the Government synthetic rubber program.

REFERENCES

[1] Wood, "Advances in Colloid Science," edited by Mark and Whitby, New York, 1946, Vol. 2, p. 57; Wood and Bekkedahl, *J. Applied Physics* **17**, 362 (1946).
[2] Gregory, Pockel and Stiff, *India Rubber World* **117**, 611 (1948).
[3] Forman, *Ind. Eng. Chem.* **36**, 738 (1944).
[4] Conant and Liska, *J. Applied Physics* **15**, 767 (1944).
[5] Beatty and Davies, *J. Applied Physics* **20**, 533 (1949).
[6] Gehman, Woodford, and Wilkinson, *Ind. Eng. Chem.* **39**, 1108 (1947); American Society for Testing Materials, "Standards on Rubber Products," 1949, p. 527.
[7] Fisher, Hollomon, and Turnbull, *J. Applied Physics* **19**, 775 (1948); Kauzmann, *Chem. Revs.* **43**, 219 (1948).
[8] Fisher, Hollomon, and Turnbull, *J. Applied Physics* **19**, 775 (1948).
[9] Wood, "Advances in Colloid Science," edited by Mark and Whitby, New York, 1946, p. 57; Gregory, Pockel, and Stiff, *India Rubber World* **177**, 611 (1948).
[10] American Society for Testing Materials, "Standards on Rubber Products", 1949, p. 527.
[11] Wood and Bekkedahl, *J. Applied Physics* **17**, 362 (1946).
[12] Morris, Hollister, and Mallard, *India Rubber World* **112**, 455 (1945).

STRESS RELAXATION OF SOME RUBBER AND SYNTHETIC RUBBER VULCANIZATES IN COMPRESSION *

J. R. BEATTY AND A. E. JUVE

B. F. GOODRICH RESEARCH CENTER, BRECKSVILLE, OHIO

Vulcanizates of rubber and synthetic rubber find wide and useful applications under conditions of compressive stress in gaskets, seals, suspension systems for vibration isolation, and other uses. In some of these applications the rubber is subjected to a load, either static or dynamic, or a combination of both. In other cases the compression strain is constant, and the resulting stress is utilized as a seal for fluids or gases. It is with this second application of rubber in compression that this work is concerned.

In the use of rubber under compression as a seal the service life is dependent on maintaining a value of stress above a minimum necessary for the seal to be effective. It can readily be seen, then, that some method of evaluating materials with respect to service life is highly desirable. Compression set tests, method A or B, of the American Society for Testing Materials[1], depending on the service conditions, have been widely used for some time in evaluating rubber materials to be used in compression. This test, however, does not give an answer which is directly applicable as to units, and the test time ordinarily used is too short. Test results are reported as percentages secured from the ratio of the unrecovered portion of the amount compressed to the amount the sample is compressed. The unrecovered portion of the amount the sample is compressed is measured after a prescribed interval at room temperature after removing the stress from the sample. A better measure of the property in question, the stress as a function of time, would be to measure this property directly.

Many excellent articles have been written on compression stress measurements of rubber[2], stress relaxation of tension samples[3], compression stress relaxation as affected by low temperature[4], and compression stress relaxation measuring devices[5]. These papers have been useful and informative in their fields, but have not applied to the problem at hand, either owing to the fact that the sample or conditions have not approximated those encountered in this particular field of application, or the breadth of the investigation has been inadequate. More information was desired on the various commercially available polymers and the effect on the compression stress relaxation of these compounded polymers of a wide temperature range, various degrees of deformation, and variations in composition. In addition, before these variables were investigated, it was necessary to determine the effect of sample shape and slippage on stress relaxation. The latter two factors would influence the choice of sample or sample construction. The effect of shape of sample and lubricated compressing surfaces has already been determined on the load-deflection characteristics[2].

* Reprinted from the *India Rubber World*, Vol. 121, No. 5, pages 537–543, February 1950. This paper was presented before the Rubber and Plastics Division of The American Society of Mechanical Engineers, New York, November 29, 1949.

TESTING EQUIPMENT

A simple tester to provide the information desired was designed and built similar to that of Blow and Fletcher[6]. Figure 1 is a photograph of the complete apparatus, and Figure 2 is a diagram of the essential parts and their operation. The tester is essentially a method of compressing a sample of predetermined percentage of its original height and measuring, by an adjustable dead weight loading, the minimum stress necessary to maintain this deflection as a function of time. As this property of rubber and rubberlike materials depends on the

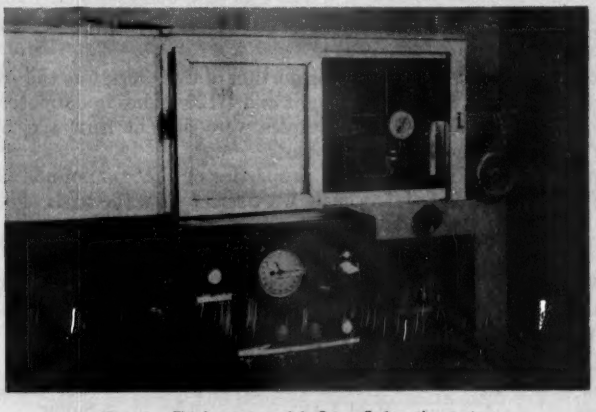


FIG. 1.—Equipment used for stress relaxation tests.

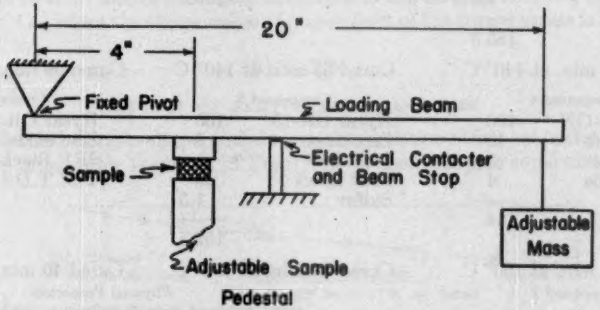


FIG. 2.—Schematic diagram of stress relaxation testing equipment.

temperature, the machine was enclosed in a temperature-controlled air oven. The maximum load which it is possible to apply to the test-specimen is 1000 pounds. To increase the number of tests which could be run simultaneously, jigs, such as shown in Figure 3, were made. These jigs made it possible to remove the sample and jig from the tester, while the desired compression was maintained on the sample, and to place the assembly in an oven at whatever temperature desired. Other tests could also be made, and the stress checked periodically by placing the jig and sample into the tester and determining the

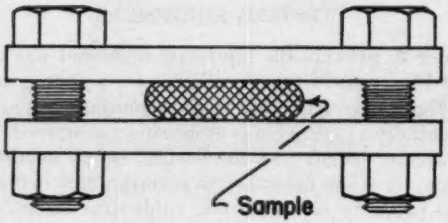


FIG. 3.—Stress relaxation testing jig.

stress to maintain the original deflection. These jigs were used exclusively for long-time tests.

The test sample used in the major portion of this work was the ASTM compression set sample, 0.500-inch in height and 1.129 inches in diameter, giving an area of one square inch. These samples were die cut from six- by ten-inch sheets of the compounded cured rubber.

Recipes, cures, and stress-strain properties of the compounds used in this work are given in Table 1. The cures were selected on the basis of stress-strain tests.

TABLE 1

RECIPES, CURES, AND TENSILE PROPERTIES OF COMPOUNDS TESTED

Compound 1		Compound 2		Compound 3	
Natural rubber	100	Natural rubber	100	GR-S 10	100
Zinc oxide	5	Zinc oxide	5	Zinc oxide	5
M.B.T.S*	1	SRF Black	80	M.B.T.S*	1.75
SRF Black	75	AgeRite Powder	1	SRF Black	65
Stearic acid	1	T.M.T.D.†	3.5	Sulfur	1.75
AgeRite Powder	1		189.5		173.5
Sulfur	2.5				
	185.5				
Cured 35 min. at 140° C		Cured 35 min. at 140° C		Cured 90 min. at 150° C	

Compound 4		Compound 5		Compound 6	
Neoprene-GN	100	Hycar OR-15	100	Hycar OR-15	100
SRF Black	45	Zinc oxide	5	Zinc oxide	5
Zinc oxide	5	M.B.T.S*	1	SRF Black	50
Mag. oxide	4	SRF Black	45	T.M.T.D.†	4
	154	Sulfur	1.5		159
			152.5		
Cured 40 min. at 150° C		Cured 40 min. at 150° C		Cured 40 min. at 150° C	

Compound 7	
GR-I	100
Zinc oxide	5
M.B.T.S*	0.5
SRF Black	60
Sulfur	2
T.M.T.D.†	1
	168.5
Cured 40 min. at 150† C	

	Physical Properties			
Cpd.	Shore A durometer	Tensile strength (p.s.i.)	Elongation (%)	300% Modulus (p.s.i.)
No. 1	64	2700	430	2150
2	61	2800	425	1650
3	64	2400	460	1600
4	66	2700	420	2300
5	65	2600	380	2100
6	63	2600	520	1700
7	58	1800	725	600

* 2-2',-Benzothiazyl disulfide
† Tetramethylthiuram disulfide

TEST PROCEDURE

Two samples are conditioned at the same time until equilibrium temperature is attained, and the free heights of the samples are measured. The sample pedestal is adjusted to give the correct compression, and the first sample is loaded in increments until the predetermined compression is secured. This operation requires about 30 to 40 seconds. This sample is discarded, and the sample pedestal is reset if necessary. The stress necessary to produce the desired reflection is then imposed on the second sample; time is measured in seconds from the moment compression starts. Thirty-six seconds, or 0.01-hour, is usually the shortest time in which it is possible to determine accurately the compression stress; so it is usually spoken of as the "zero" time. Successive readings are in approximately a geometric progression from 0.01-hour, as the curve of stress relaxation is approximately a straight line when plotted against logarithmic time.

At the start of this program it was arbitrarily decided that when the value of S_t/S_o, or the stress at time t, reached 50 per cent of the initial stress (at 0.01-hour), the test would be considered complete. This is probably much too soon if measurements of actual service life are to be made, as less than 50 per cent of the initial stress would, in many instances, perform the job required. However many of these tests would have continued for such long times that the value of such data is doubtful, and it is thought that estimates of service life based on the 50 per cent value are reasonably valid.

ACCURACY

The stress on the sample may be determined to ± 0.5 pound, and, as it is rare for the stress to go below 100 pounds, the maximum error in the determinations is in the order of 1 per cent. In most determinations the possible error is never more than one-half this, as the stress is 200 pounds or more at the end of the test, *i.e.*, when the stress value of 50 per cent of the initial stress is attained.

RESULTS

EFFECT OF SAMPLE SHAPE AND SIZE

The effect of sample shape and size on compression stress relaxation for five geometries of samples is shown in Figure 4. These samples consisted of a cyl-

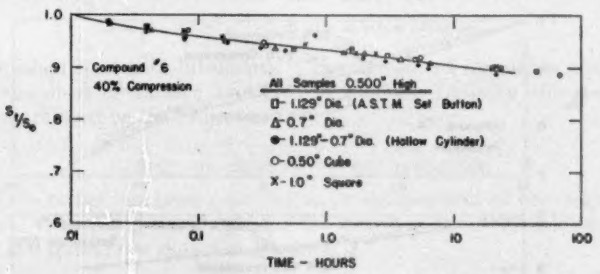


FIG. 4.—Effect of sample shape on stress relaxation results.

inder 1.129-inch in diameter by 0.5-inch high (ASTM compression set button), a cylinder 0.7-inch in diameter by 0.5-inch high, a hollow cylinder 1.129-inch

outside diameter and 0.7-inch inside diameter by 0.5-inch high, a rectangular piece one- by one- by 0.5-inch high, and a 0.5-inch cube.

EFFECT OF SLIPPAGE

Figure 5 shows some typical data obtained with 1.129-inch diameter by 0.5-inch high samples, bonded to steel, against polished steel with no bond, and

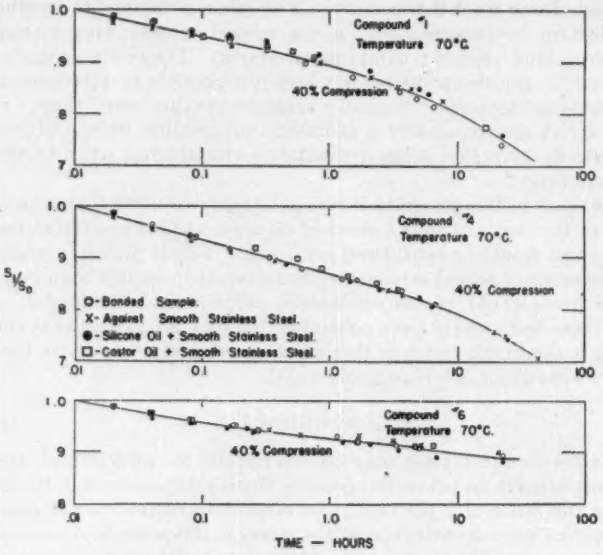


FIG. 5.—Effect of type-test surface on stress relaxation results.

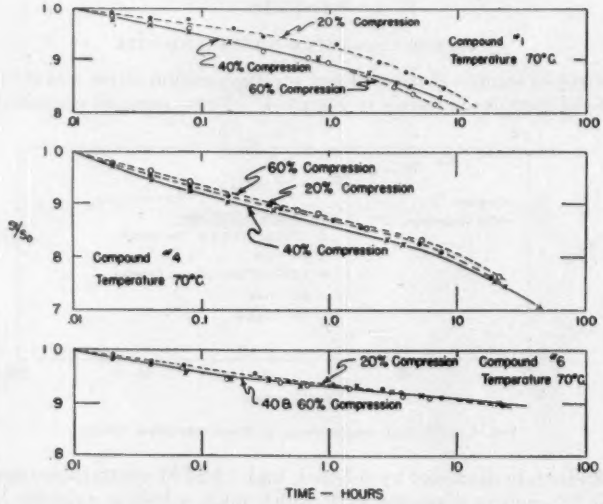


FIG. 6.—Effect of degree of deformation of sample on test results.

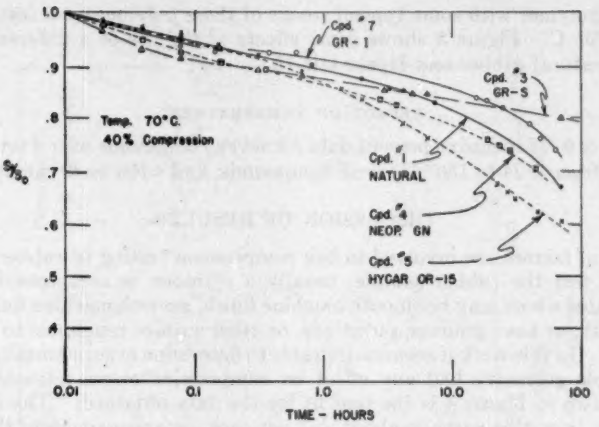


FIG. 7.—Effect of type-polymer on test results.

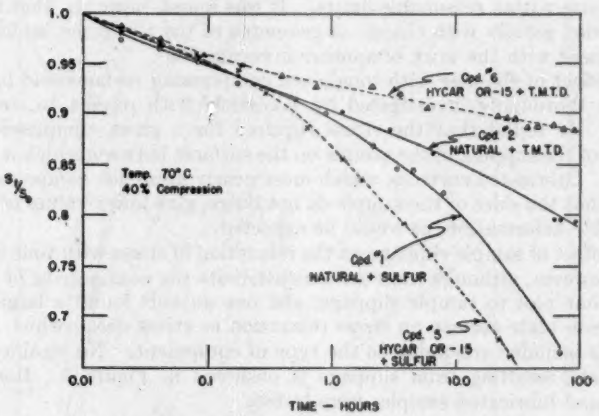


FIG. 8.—Effect of type of cure on stress relaxation.

smooth polished steel with lubricants. The agreement for any one compound is good regardless of surface friction. A medium-viscosity silicone oil and castor oil were used as the lubricants.

EFFECT OF DEGREE OF DEFORMATION

Stress relaxation has been reported to be independent of the degree of deformation[7]. This point was checked in the course of the investigation reported here, and the results are shown in Figure 6.

EFFECT OF POLYMER

Stocks of natural rubber, GR-S 10, Neoprene-GN, Hycar OR-15 and GR-I were prepared according to the recipes of Table 1. They were compounded to have a hardness range of 60 ± 5 points Shore A durometer. Figure 7 shows the

effect of polymer with some typical stocks of these polymers at a test temperature of 70° C. Figure 8 shows some effects of the use of a different type of cure on natural rubber and Hycar OR-15.

EFFECT OF TEMPERATURE

Figures 9–15 inclusive present data for seven compounds over a temperature range of from +24 to 150° C for all compounds, and a few tests run at −25° C.

DISCUSSION OF RESULTS

Several factors are involved in the compression testing of rubber. In the ordinary test the rubber sample, usually a cylinder, is compressed between metal plates which may be smooth machine finish, smooth machine finish with a high polish, or have grooves, serrations, or other surface roughness to minimize slippage. In this work it seemed desirable to determine experimentally whether the sample geometry had any effect on compression stress relaxation. The curve drawn in Figure 4 is the best fit for the data obtained. The maximum deviation from this curve is about ±1 per cent, or approximately the experimental error; so it is concluded that stress relaxation is independent of sample shape or size within reasonable limits. It was found, however, that the initial stress varied greatly with change in geometry of the test piece, which point is in agreement with the work of another investigation[3].

The effect of slippage with roughened compressing surfaces and lubrication has been thoroughly investigated by Kimmich[2] with respect to compression loading. He found that the stress required for a given compression was a function of the slipping of the sample on the surfaces between which it was compressed. Lubricated surfaces, which most nearly approach compression stress only, in that the sides of the sample do not bulge, give lower values of stress for comparable deformation, as would be expected.

The effect of sample slippage on the relaxation of stress with time is not well known however, although some authors attribute the nonlinearity of the stress *vs.* log. time plot to sample slippage, and one author[8] found a large effect of compression plate surface on stress relaxation or stress decay which in his experiments included creep due to the type of equipment. No significant trend in the data resulting from slippage is observed in Figure 5. Bonded, unbonded, and lubricated samples were tested.

DEGREE OF DEFORMATION

Tests made in the laboratory, results of which are shown in Figure 6, show no effect of degree of deformation. A maximum deviation from the mean of about ±2 per cent was found in one case, that of Compound No. 1. The other results shown in this figure have less deviation from the mean, about ±1 per cent, which error might easily result from experimental error and differences between samples.

EFFECT OF POLYMER

In Figure 7 it is seen that the materials arrange themselves in various orders of superiority, depending on the time at which the curves are observed. The GR-S stock, Compound No. 3, is the only stock giving essentially a straight line for values on this plot. The differences between compounds observed early in the test period are influenced largely by the elasticity of the rubber, while the departure of the curves from a straight line seems to indicate the effect of

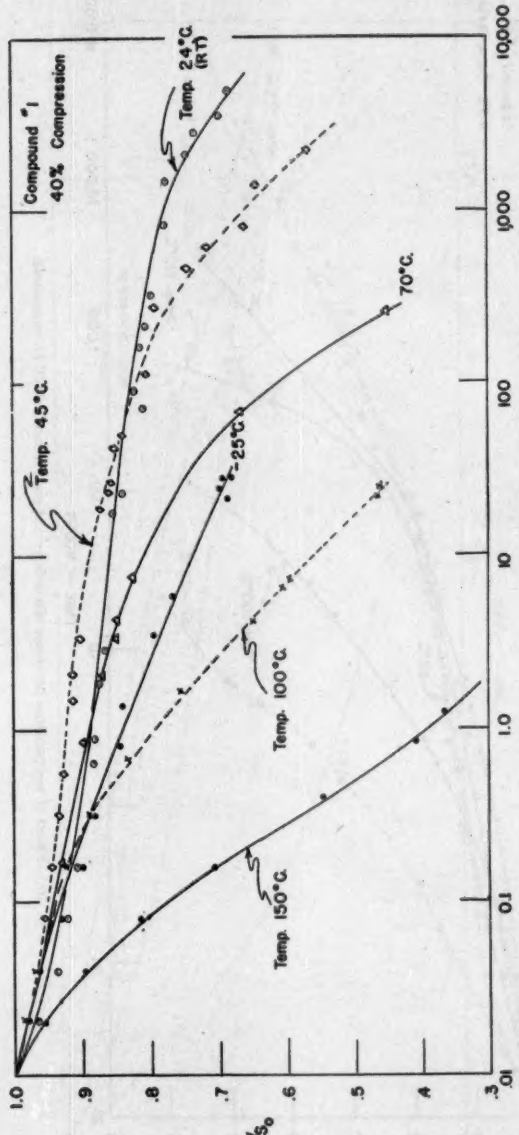


FIG. 9.—Effect of temperature on stress relaxation—natural rubber-sulfur compound.

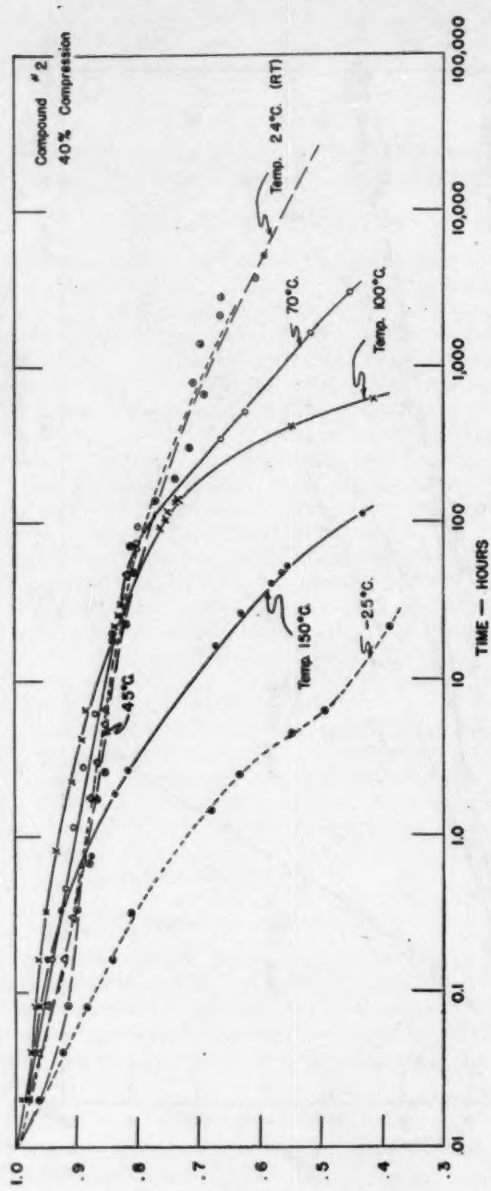


FIG. 10.—Effect of temperature on stress relaxation—natural rubber-T.M.T.D. compound.

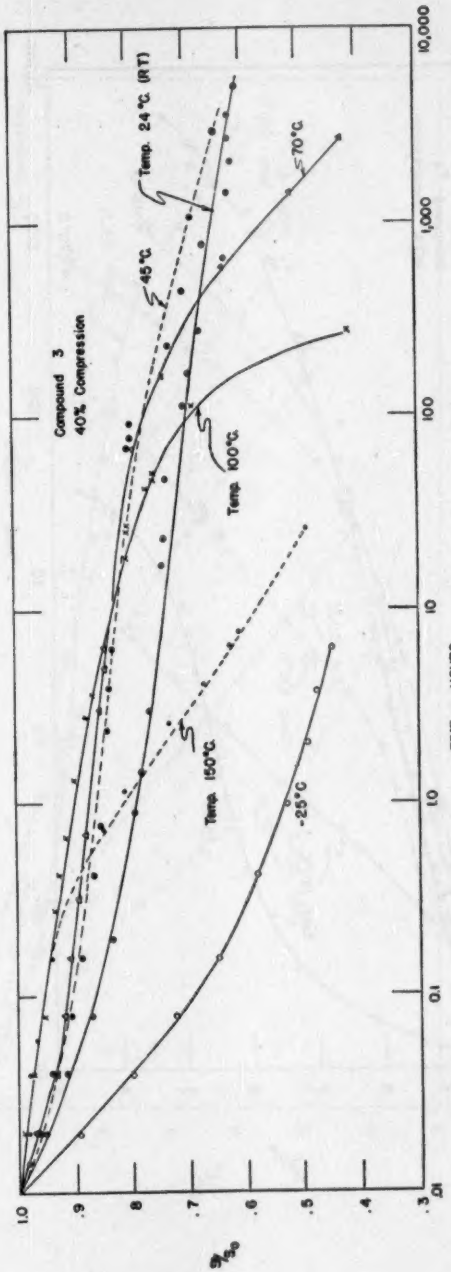


FIG. 11.—Effect of temperature on stress relaxation—GR-S-10-sulfur compound.

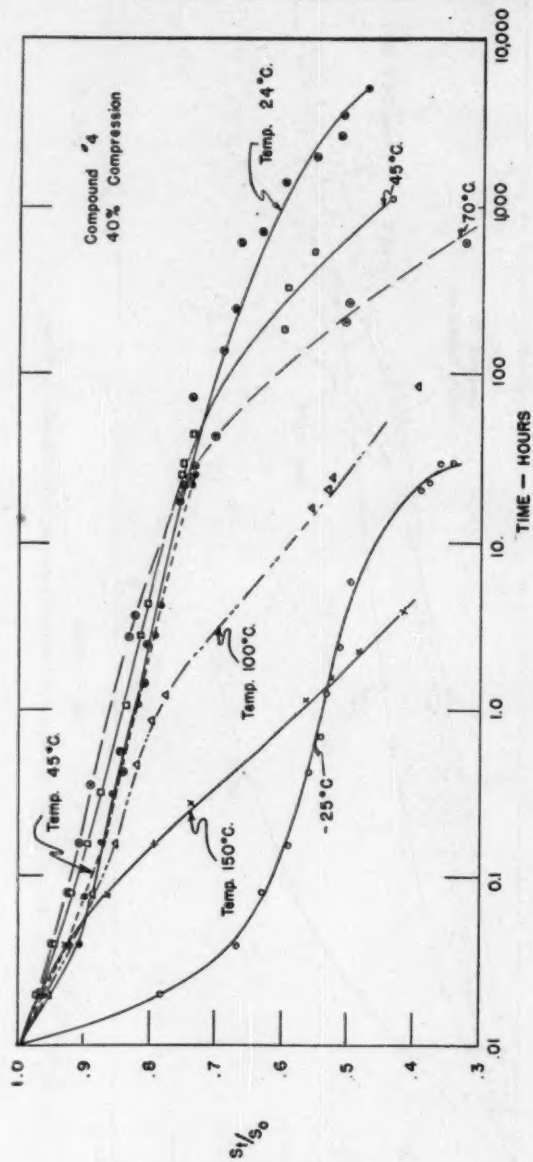


FIG. 12.—Effect of temperature on stress relaxation—Neoprene GN compound.

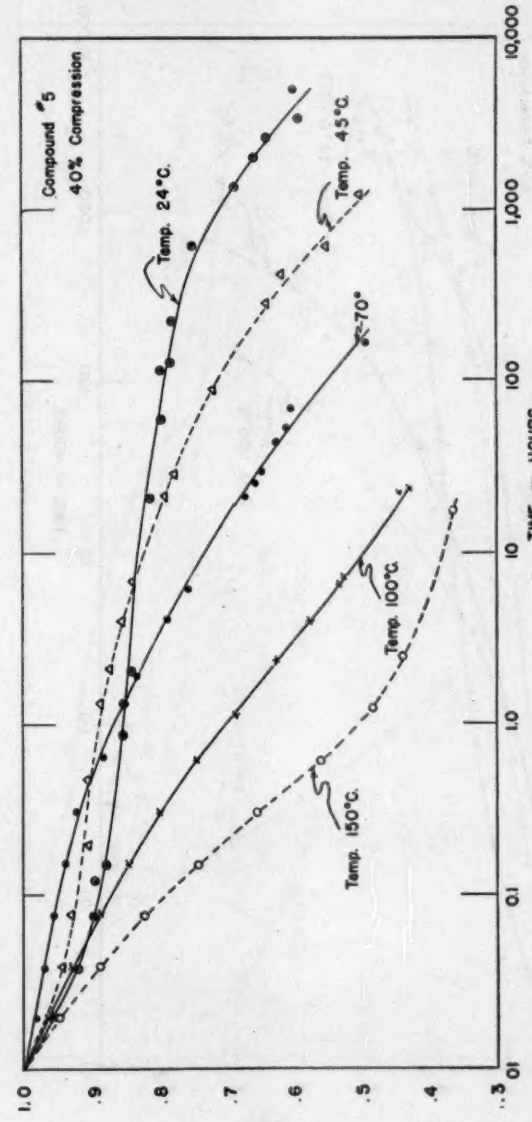


FIG. 13.—Effect of temperature on stress relaxation—Hycar OR-15-sulfur compound.

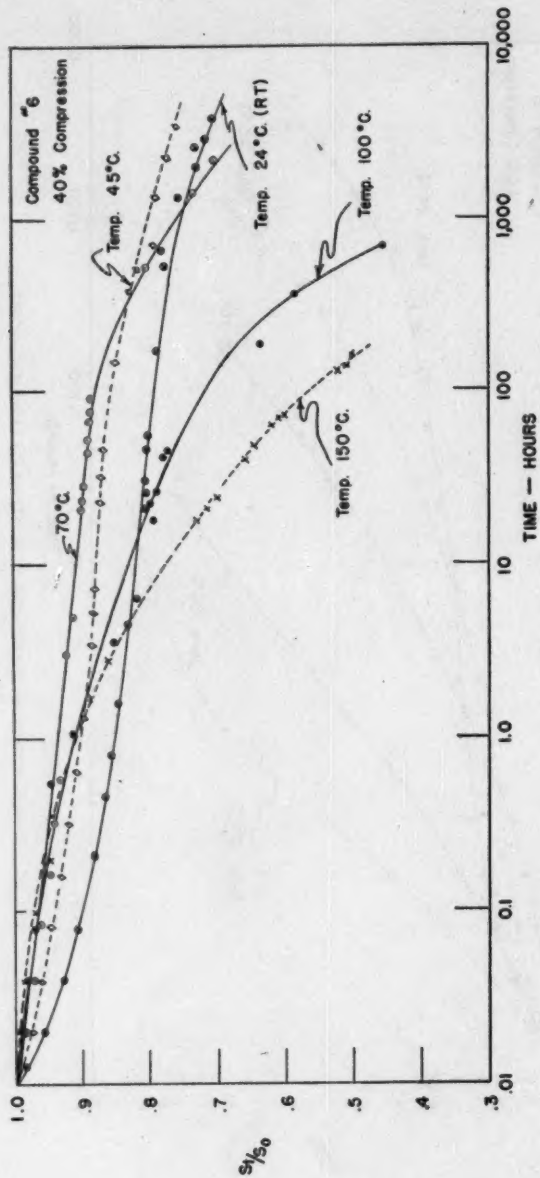


FIG. 14.—Effect of temperature on stress relaxation—Hycar OR-15-T.M.T.D. compound.

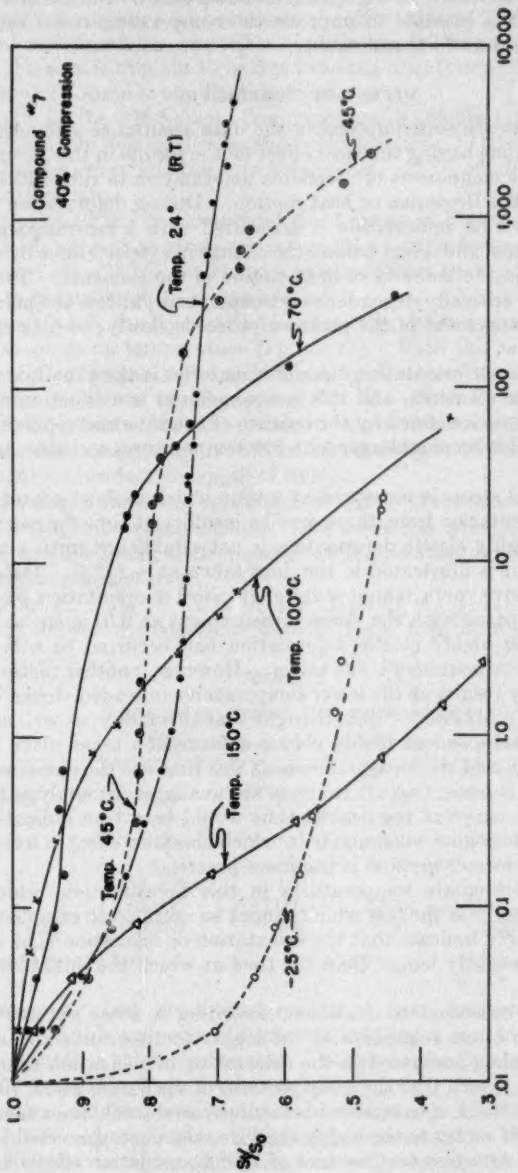


FIG. 15.—Effect of temperature on stress relaxation—GR-I compound.

oxidation on the rubber. In Figure 8 it is shown that by the use of a particular nonsulfur cure it is possible to improve the compression stress relaxation of both Hycar OR-15 and natural rubber.

EFFECT OF TEMPERATURE

Several effects are superimposed in the data secured as a function of temperature[9]. The one having the most effect on the results in this investigation is the highly elastic component of reversible deformation in rubberlike materials associated with the Brownian or heat motion. During deformation the highly elastic component of deformation is associated with a rearrangement of the structural elements, and it lags behind the change in external force by an amount which depends on the mobility of heat motion of the elements. The heat motion in rubber is critically dependent on temperature; at low temperatures it is small, and rearrangement of the particles proceeds slowly; so high elasticity is suppressed.

The relaxation or orientation time of a material is the time taken for rearrangement of the elements, and this rearrangement is a function of the heat motion. This time is defined by the balance of cohesive and repulsive forces in the material, and it becomes larger with low temperatures and shorter with high temperatures.

If the applied stress is measured at a time which is short compared to the relaxation or orientation time, there may be insufficient time for rearrangement to occur, and highly elastic deformation is not established until a much later time. This point is illustrated in the data taken at −25° C. Data taken at temperatures above room temperature show shorter orientation or relaxation times when compared with the stress measurement at 0.01 hour, as shown by the fact that the highly elastic deformation had occurred to a large extent before the stress measurement was taken. However, another factor which influences the early results at the lower temperatures in loaded stocks is the filler effect reported by Mullins[10]. It is thought that this factor, as well as the time- and temperature-dependent highly elastic deformation takes place very early in the test period, and the measurements at this time are the combined effect of the two. On this basis, two alternatives are available for analyzing the data. The slope of the curve at the desired time would be a true indication of performance, or a pure-gum vulcanizate in which the filler effect is avoided could be tested. The former method is the more practical.

Data at intermediate temperatures in this investigation, which show a change in slope early in the test which cannot be ascribed to sample slippage or oxidation, probably indicate that the orientation or relaxation time of the rubber and filler is slightly longer than the time at which the initial stress (S_o) is measured.

The relative resistance to oxidation, according to some authors[3], accounts for differences in stress relaxation at the higher temperatures and after times which are long when compared to the orientation or relaxation time.

In Figure 9 it is seen that the early portions of the curves at 45, 70, and 100° C for Compound No. 1, a natural-rubber sulfur-cured stock, are above the room temperature curve owing to the highly elastic component of reversible deformation in rubber. At a test temperature of 150° C, oxidation effects are marked from inception of the test. The relatively high values of S_t/S_o compared to the other materials tested at −25° C for this compound are due to its short orientation time and small modulus change due to low temperature.

Compound No. 2, a natural rubber stock cured with tetramethylthiuram disulfide, exhibits superior properties to a sulfur cure at high temperatures. This type of cure minimized the effect of oxidation. The poor performance at −25° C in this case is thought to be due to a long orientation time, and in addition there may be some crystallization effects.

The results for the GR-S stock, Compound No. 3 (Figure 11), show the same general temperature dependence as the previous curve. Oxidation effects are not so marked, however, and the data obtained at −25° C are due entirely to the long orientation time.

The oxidation effects on Compound No. 4 shown in Figure 12 are not great. The material is subject to stress-relaxation; the rate is dependent on the test temperature. At −25° C, the curve shows a decided change in slope after 10 hours, which is attributed to crystallization.

Compound No. 5, the Hycar OR-15 sulfur cure, shows a marked dependence of stress relaxation on temperature (Figure 13). With this same polymer the temperature effect seems to be minimized by a tetramethylthiuramdisulfide cure as shown in Figure 14 (Compound No. 6). With Compound No. 6 in particular it will be noted that the increased rate of oxidation usually found due to raising the test temperature is resisted successfully in the case of the 45 and 70° C tests for a considerable length of time.

Figure 15 shows the stress relaxation of GR-I, Compound No. 7, as being very much dependent on temperature. The stress relaxation at room temperature is low, but increasing or decreasing the temperature increases the rate of stress relaxation considerably.

Table 2 summarizes the data on the effect of temperature on the stress relaxation of the seven compounds tested. From this table it is readily seen

TABLE 2

SUMMARY OF STRESS RELAXATION DATA

Compound No.	Time in hours $S \pm / S_I$ to reach 0.7 at temperatures of:					
	25° C	24° C	45° C	70° C	100° C	150° C
1	21	4,000	700	50	2.7	0.16
2	1.2	700	700	220	185	13.
3	0.1	100	700	300	100	3.0
4	.67	83	83	45	3.1	0.3
5	..	1,200	130	16	1.0	0.25
6	..	*50,000	*15,000	2,100	130	27.02
7	0.02	3,500	400	80	5.2	.165

* These figures are extrapolated.

that a compound which gives good results at room temperatures does not necessarily retain this property at high temperature or low temperature when compared to another rubber compound. For example, Compounds No. 1 and No. 2 or No. 2 and No. 7 show this markedly.

Experimental results herein reported do not agree in all respects with those reported by Tobolsky *et al.*[4] who utilized ring specimens of small cross-section in tension. The lack of agreement is undoubtedly due to the relatively large volume/surface area ratio of the samples used in this investigation which prevents the attainment of equilibrium conditions.

CORRELATION BETWEEN COMPRESSION SET AND COMPRESSION STRESS RELAXATION

There was the possibility that compression set tests conducted by ASTM D-395-47T, method B might correlate with compression stress relaxation results, as the property is at least partially involved in both tests. Table 3 com-

TABLE 2

CORRELATION BETWEEN COMPRESSION STRESS RELAXATION AND COMPRESSION SET AT 40% COMPRESSION

Compound No.	Compression set at 22 hours at 70° C (%)	Rank	Compression stress relaxation at 22 hours at 70° C (%)	Rank	Compression stress relaxation at 70° C after 100 hours (%)	Rank
1	35	6	24	4	38	5
2	13	2	17	2	21	2
3	14	3	18	3	22	3
4	34	5	26	5	38	5
5	34	5	33	6	45	6
6	9	1	15	1	12	1
7	15	4	18	3	34	4

pares results from the two types of tests on the same rubber compounds with identical conditions of temperature and deformation. The values for stress relaxation are actually $(1-S_t/S_o)$, or the percentage stress lost rather than the percentage stress retained ordinarily used. This makes the numbers correspond more closely, as set tests measure the percentage of height lost over the test period. The correlation is just fair, but considering variables of the compression set tests that is to be expected. The same general trend in rating the compounds is noted, however, in both test methods.

REFERENCES

[1] American Society for Testing Materials, Book of A.S.T.M. Standards, 1947 Supplement, Part III-B, D-395-47T, methods A and B, p. 220.
[2] Kimmich, *India Rubber World* **103**, No. 3, 45 (1940).
[3] Tobolsky, Prettyman, and Dillon, *J. Applied Physics* **15**, 380 (1944).
[4] Phillips and Labbe, *India Rubber World* **119**, 224 (1948).
[5] McDonald and Ushakoff, *Anal. Chem.* **20**, 713 (1948); Morris, Jones, and Seegman, *India Rubber World* **119**, No. 4, 466 (1949).
[6] Blow and Fletcher, *India Rubber J.* **106**, 403 (1944).
[7] Tobolsky, Prettyman, and Dillon, *J. Applied Physics* **15**, 380 (1944); McDonald and Ushakoff, *Anal. Chem.* **20**, 713 (1948).
[8] Thorn, *ASTM Bulletin* **112**, 13 (1941).
[9] Aleksandrov and Lazurkin, *Acta Physicochem.* (U.R.S.S.) **12**, 648 (1940); "Rubber in Engineering," Chemical Publishing Co., Brooklyn, **1946**, p. 10.
[10] Mullins, *J. Rubber Research* **16**, 12 (1947); *India Rubber World* **120**, No. 1, 63 (1949).

MECHANISM OF REËNFORCEMENT. III. VISCOSITY OF CARBON BLACK SUSPENSIONS IN GR-S SOLUTIONS *

LEONARD E. AMBORSKI AND GEORGE GOLDFINGER

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BUFFALO, BUFFALO, N. Y.

INTRODUCTION

Rehner[1] and Smallwood[2] attempted to describe the effect of rigid filler particles on the modulus of elasticity of an elastomer in which small amounts of this filler are dispersed. The calculations of both authors led to the same equation:

$$E = E_0 (1 + 2.5\ C) \tag{1}$$

where E is the modulus of elasticity of the sample containing the filler, E_0 the modulus of the corresponding pure gum stock, and C the volume concentration of the filler. This equation is similar to the well known Einstein equations[3]. Working by analogy with the problem of viscosity of suspensions, Guth and Gold[4] proposed the same equation, to which he added the square term of the Einstein equation:

$$E = E_0 (1 + 2.5\ C + 14.1\ C^2) \tag{1a}$$

The conditions for the validity of this relationship are that: (1) the filler particles are rigid; (2) they are spherical; (3) the elastomer adheres to the filler particles; and (4) the particles are large compared to the discontinuity of the matrix. Condition (1) is certainly fulfilled; conditions (2) and (3) are probably sufficiently closely fulfilled so as not to cause undue difficulties, but condition (4) is certainly not fulfilled, since we are dealing with a vulcanized matrix whose structural elements are comparable in size to the filler particles in question.

Nevertheless, this effect of a wide variety of fillers on the modulus of elasticity of elastomers can be satisfactorily predicted, particularly by the relationship (1a), proposed by Guth.

However, the effect of reënforcing carbon blacks is significantly higher than the predictions of Equation (1a), (see Figure 1). Assuming, tentatively, that the Rehner-Smallwood-Guth relationship should hold despite the objection mentioned above, a combination of two effects can account for the unique behavior of carbon-black loaded samples.

(1) It has been shown that carbon black adsorbs preferentially certain fractions of rubber and that the fraction of the matrix between carbon black particles has a higher modulus than the original gum stock used[5].

(2) The volume of the carbon black is increased by this adsorbed layer of rubber; hence, the volume, C, is larger than the volume of carbon black as added.

* Reprinted from the *Recueil des Travaux Chimiques des Pays-Bas*, Vol. 68, No. 10, pages 733–744 September–October 1949. This paper contains some of the experimental work carried out by L. E. Amborski in partial fulfilment of the requirements for a degree of Doctor of Philosophy. Gratitude is expressed for the financial assistance received through the Frederick Gardner Cottrel Grant-in-Aid of Postwar Scientific Research, without which this work would not have been possible.

In view of the remarkable experimental success of Equation (1a) in cases not involving carbon black, it is of obvious interest to gain added information on the nature of the rubber layer surrounding the carbon black particle. This was achieved by investigating the viscous properties of suspensions of carbon black in GR-S solutions. Thus information was gained on the thickness of the rubber layer, its rigidity, and the shift in the concentration of rubber with respect to

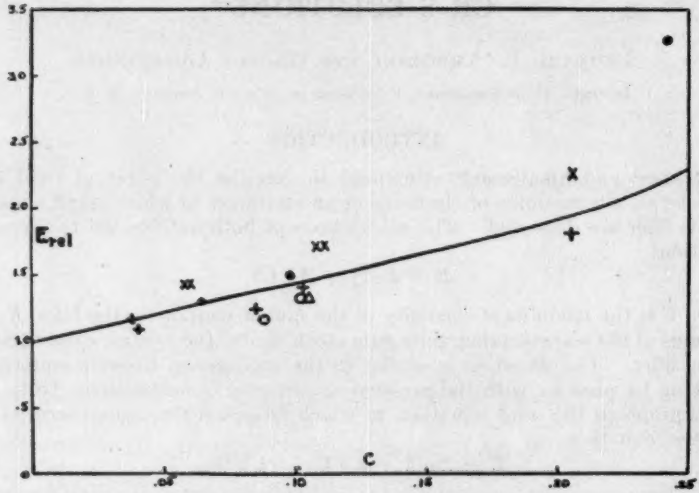


FIG. 1.—Relative modulus of elasticity plotted against concentration of fillers. Experimental data of Smallwood indicated by: ● Channel black, ○ P-33, Thermax, × Kadox, ×× Zinc oxide, + Gilders' whiting, △ Catalpo clay. The curve is drawn from Equation 1a.

solvent, compared to the concentration of the solution in adsorption equilibrium with the rubber covered carbon black surface. By applying the relation,

$$\eta = \eta_0 (1 + 2.5\ C + 14.1\ C^2) \qquad (2)$$

(in which η is the viscosity of the suspension, and η_0 the viscosity of the rubber solution), the actual volume, C, could be determined if the conditions fulfilled the assumptions of the equation. However, the carbon black spheres surrounded by rubber certainly are not rigid, and it is doubtful whether the rubber solution can be considered continuous. By carrying out viscosity measurements at various rates of shear and extrapolating to zero rate of shear, both of these difficulties can be eliminated or at least minimized.

EXPERIMENTAL

Three two-liter stock solutions were prepared from purified commercial GR-S and xylene to give 1, 1.5, and 2 grams of GR-S per 100 cc. of solution (at room temperature), respectively. To five 100-cc. portions from each of these three solutions 0.5, 1, 2, 4, and 8 grams, respectively, of Cabot Grade 6 easy processing channel black (approximately 100 sq. m. per g. surface area) were added, giving the following combinations as listed in Table I).

These fifteen samples were violently agitated for 8 to 10 days and stored in darkness at approximately 0°C in airtight containers, together with the remaining original stock solutions.

TABLE I

COMPOSITION OF SAMPLES AND RATIOS OF GR-S TO CARBON BLACK

GR-S per 100 cc. solution \ Carbon Black per 100 cc. solution	0.5 g.	1.0 g.	2.0 g.	4.0 g.	8.0 g.
1.0 gram	2	1.0	0.50	0.25	0.125
1.5 grams	3	1.5	0.75	0.375	0.1875
2.0 grams	4	2.0	2.0	0.500	0.250

All viscosities were measured with a modified rotating-cylinder Stormer type viscometer. It consist of a strainless steel cup immersed in a constant temperature bath of 22.5° C. A solid rotating aluminum cylinder is driven through a jewel-bearing gear train by a falling weight. The dimensions of the viscometer are as follows:

Liquid cup, diameter 4.742 cm.
Rotating cylinder, diameter 4.50 cm., height 3.50 cm.
Clearance between cylinder and cup, between cylindrical surfaces, 0.121 cm., at the bottom 1.5 cm.
Effective shear area, 49.455 sq. cm. Forty-four cc. of liquid is required for a measurement.

The rate of shear was varied by changing the falling weight which drives the rotating cylinder. The viscosity was obtained (in arbitrary units) by timing with an electrically actuated stopclock the time necessary for one-hundred revolutions of the cylinder and then computing the number of revolutions per minute.

To obtain the viscosity (and concentration) of the GR-S solutions after some of the rubber had been adsorbed by the carbon black, the suspensions

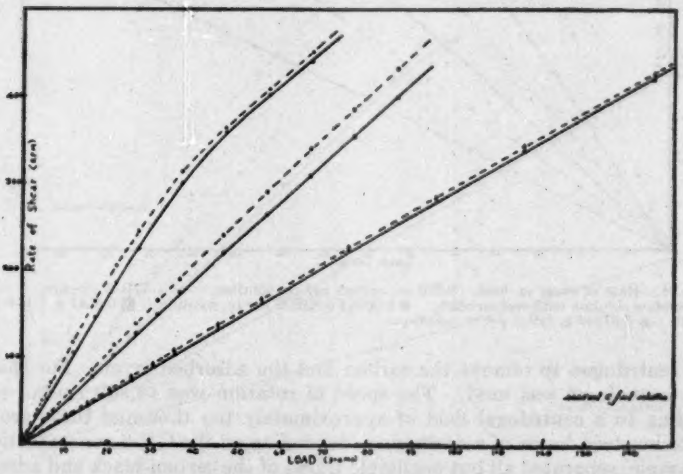


FIG. 2.—Rate of shear *vs.* load. 0.0025 cc. carbon per cc. solution. – – – –GR-S solution. ——— corresponding solution with carbon black. ● 0.00960 g. GR-S per cc. of solution. ■ 0.0147 g. GR-S per cc. of solutions. ▲ 0.01988 g. GR-S per cc. of solution.

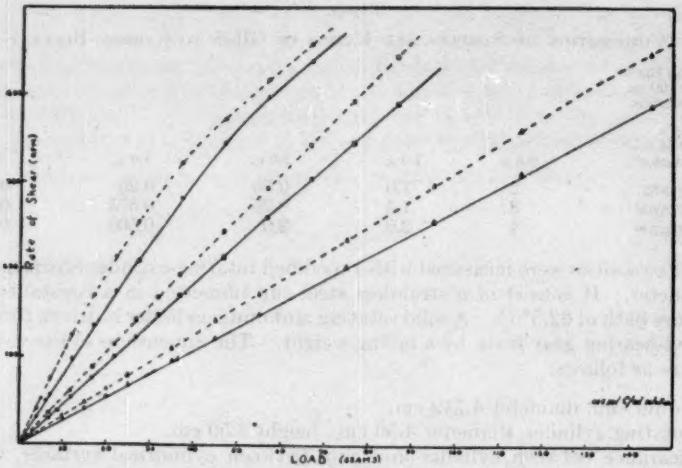


FIG. 3.—Rate of shear vs. load. 0.005 cc. carbon per cc. solution. – – – –GR-S solution. ——— corresponding solution with carbon black. ● 0.00937 g. GR-S per cc. solution. ■ 0.0145 g. GR-S per cc. solution. ▲ 0.01965 g. GR-S per cc. solution.

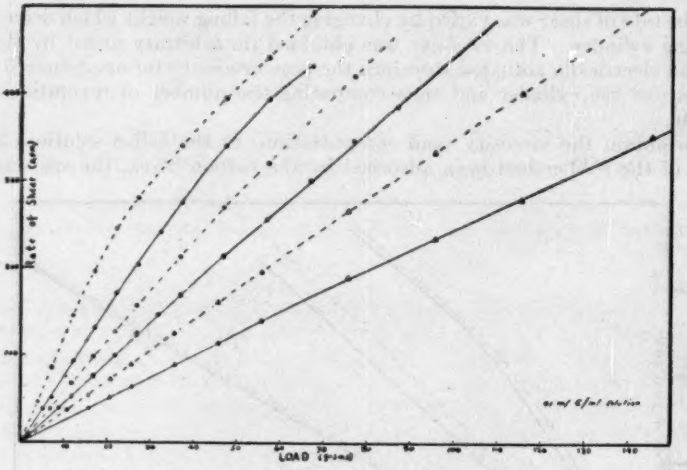


FIG. 4.—Rate of shear vs. load. 0.010 cc. carbon per cc. solution. – – – –GR-S solution. ——— corresponding solution with carbon black. ● 0.00915 g. GR-S per cc. solution. ■ 0.0141 g. GR-S per cc. solution. ▲ 0.01946 g. GR-S per cc. solution.

were centrifuged to remove the carbon and the adsorbed layer. For this, an angle centrifuge[6] was used. The speed of rotation was 13,500 r.p.m., corresponding to a centrifugal field of approximately ten thousand times gravity. Ten to fourteen hours of centrifuging (depending on the GR-S concentration of the sample) separated all but negligible traces of the carbon black and adsorbed rubber, giving a transparent supernatant solution. Solvent losses by evaporation during centrifuging were determined by weighing and corrected by the

addition of the lost amount. It was assumed that no significant shifts in distribution of the GR-S between adsorbed phase and solution occurred because of the concentration shift of carbon black in rubber as a result of centrifuging.

Viscosities were measured on the suspensions and the supernatant solutions after they reached temperature equilibrium. The results for each of the thirty samples were plotted as actuating weight in grams against the corresponding rate of shear expressed as the number of revolutions per minute (1 r.p.m. cor-

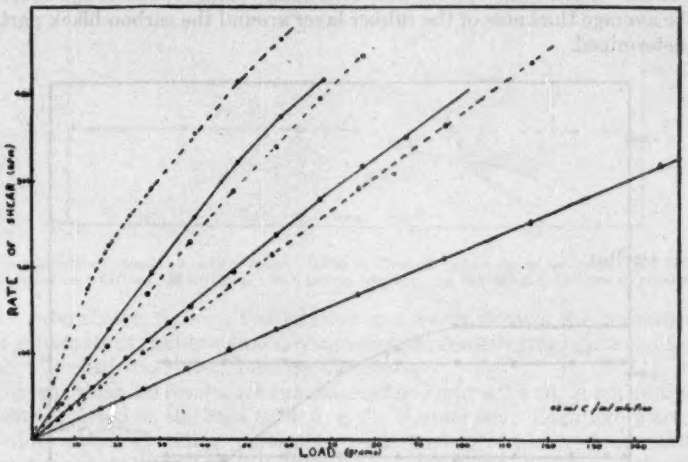


FIG. 5. Rate of shear vs. load. 0.020 cc. carbon per cc. solution. - - - -GR-S solution. ——— corresponding solution with carbon black. ● 0.00902 g. GR-S per cc. solution. ■ 0.0141 g. GR-S per cc. solution. ▲ 0.01926 g. GR-S per cc. solution.

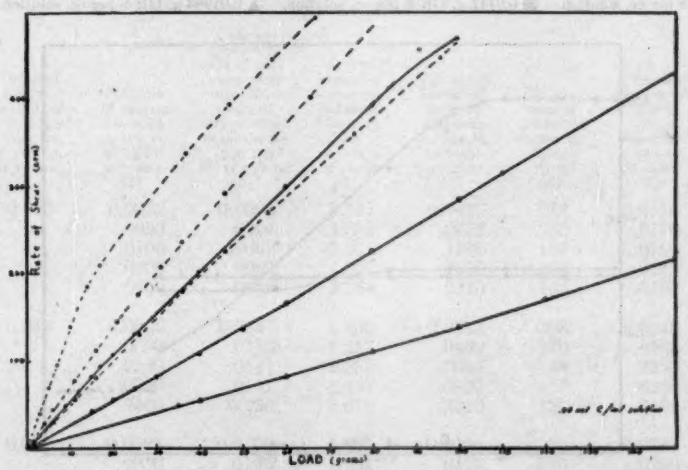


FIG. 6.—Rate of shear vs. load. 0.040 cc. carbon per cc. solution. - - - -GR-S solution. ——— corresponding solution with carbon black. ● 0.00877 g. GR-S per cc. solution. ■ 0.0136 g. G-RS per cc. solution. ▲ 0.01904 g. GR-S per cc. solution.

responds to a rate of shear of 0.0595 sec^{-1}). By interpolation, viscosities (in arbitrary units) were obtained for equal rates of shear (equal number of revolutions per minute) for pairs of samples consisting of a carbon black suspension and the corresponding supernatant rubber solution of the same sample. The ratios of the two sets of results were given as the relative viscosities. Inserting these values in Equation (2) the apparent volume of carbon black surrounded by rubber was obtained. Those values extrapolated to zero rate of shear were taken as the "true volume", from which the total volume of adsorbed rubber and also the average thickness of the rubber layer around the carbon black particles were determined.

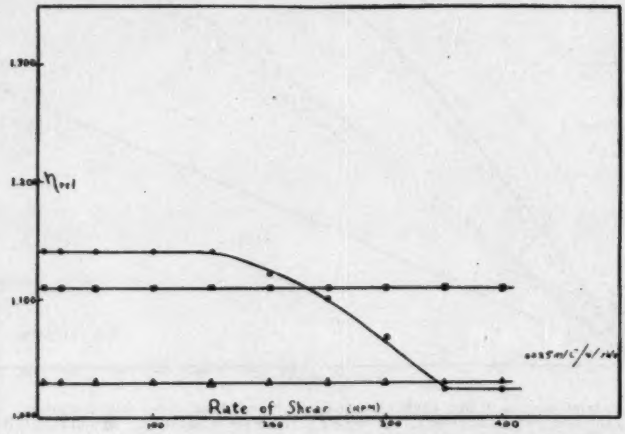


FIG. 7.—Relative viscosity vs. rate of shear. 0.0025 cc. Grade 6 carbon per cc. solution. ● 0.00960 g. GR-S per cc. solution. ■ 0.0147 g. GR-S per cc. solution. ▲ 0.01988 g. GR-S per cc. solution.

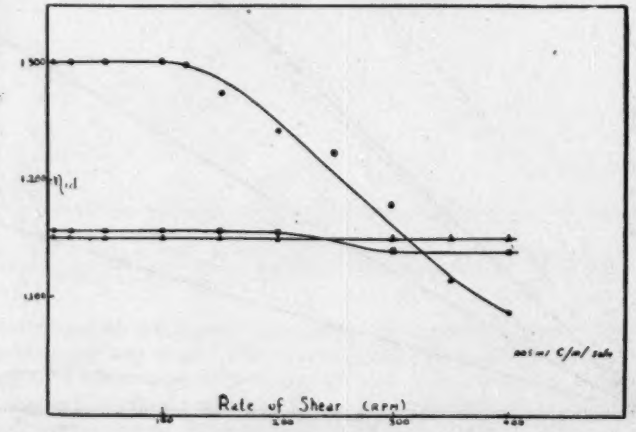


FIG. 8.—Relative viscosity vs. rate of shear. 0.0050 cc. Grade 6 carbon per cc. solution. ● 0.00937 g. GR-S per cc. solution. ■ 0.0145 g. GR-S per cc. solution. ▲ 0.01965 g. GR-S per cc. solution.

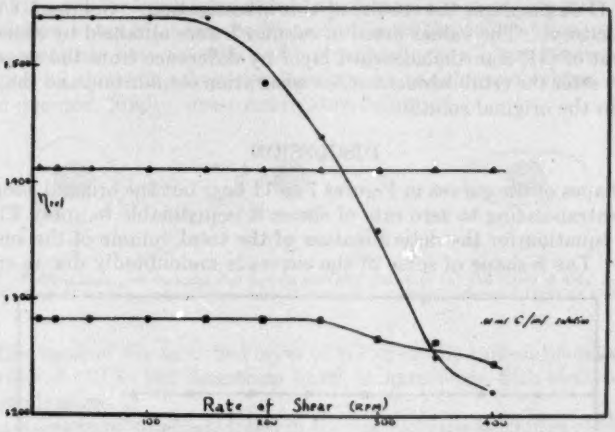


FIG. 9.—Relative viscosity *vs.* rate of shear. 0.010 cc. Grade 6 carbon per cc. solution. ● 0.00915 g. GR-S per cc. solution. ■ 0.0141 g. GR-S per cc. solution. ▲ 0.01946 g. GR-S per cc. solution.

By determining through evaporation in a vacuum oven the concentration of the supernatant rubber solution obtained from centrifuging, the weight of the rubber adsorbed was determined by difference.

The experimental results are summarized in Figures 2 to 6, in which the rate of shear is plotted *vs.* the load actuating the viscometer. Each figure contains the values obtained with a particular concentration of carbon black at three different concentrations of GR-S. From these fifteen pairs of curves, the values reported in Figures 7 to 11 were calculated. In these the relative viscosities are plotted against rate of shear.

TABLE II

Original concentration of GR-S solution in g. per cc. of xylene (1)	Volume of carbon black in cc. per cc. of GR-S solution (2)	Concentration of GR-S solution after establishment of adsorbtion equilibrium in g. per cc. of xylene (3)	η rel as obtained by extrapolating viscosity values to zero rate of shear (4)	Volume of adsorbed layer of GR-S in cc. per cc. of total solution (5)	Thickness of adsorbed layer of GR-S in Å (6)	Concentration of GR-S in adsorbed layer in g. per cc. of layer (7)
0.010	0.0025	0.0096	1.142	0.0425	242	0.0188
	.0050	.0094	1.302	.0772	230	.0176
	.0100	.0092	1.541	.1160	198	.0166
	.0200	.0090	1.867	.1550	160	.0155
	.0400	.0088	2.764	.2370	136	.0132
0.015	0.0025	0.0147	1.100	0.0312	208	0.0256
	.0050	.0145	1.157	.0400	170	.0263
	.0100	.0141	1.283	.0685	148	.0253
	.0200	.0141	1.457	.0920	117	.0240
	.0400	0.136	2.610	.2210	129	.0199
0.020	0.0025	0.0199	1.030	0.0090	99	0.0333
	.0050	.0196	1.151	.0423	170	.0280
	.0100	.0195	1.412	.0940	177	.0245
	.0200	.0193	1.705	.1320	145	.0250
	.0400	.0190	3.683	.3170	160	.0220

Table II summarizes the results of this investigation. Columns 1 to 6 are self-explanatory. The values listed in column 7 were obtained by determining the amount of GR-S in the adsorbed layer by difference from the amount left in solution after the establishment of the adsorption equilibrium and the amount of GR-S in the original solution.

DISCUSSION

The shapes of the curves in Figures 7 to 11 bear out the original assumption that, by extrapolating to zero rate of shear, it is justifiable to apply Einstein's viscosity equation for the determination of the total volume of the suspended particles. The S-shape of some of the curves is undoubtedly due to sufficient

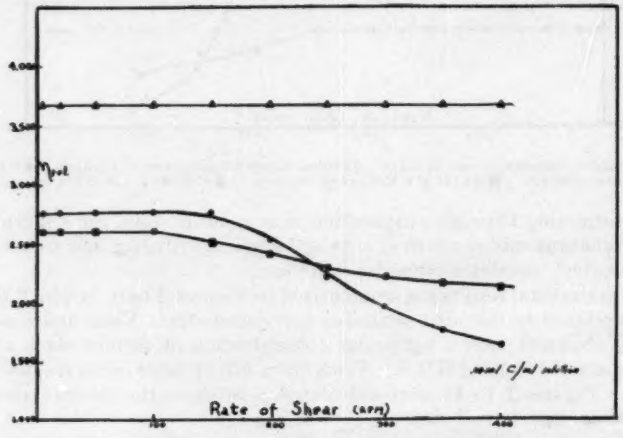


FIG. 10.—Relative viscosity *vs.* rate of shear. 0.020 cc. Grade 6 carbon per cc. solution. ● 0.00902 g. GR-S per cc. solution. ■ 0.0141 g. GR-S per cc. solution. ▲ 0.01926 g. GR-S per cc. solution.

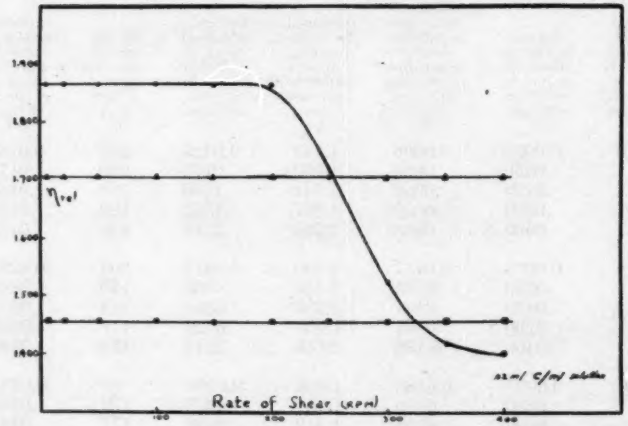


FIG. 11.—Relative viscosity *vs.* rate of shear. 0.040 cc. Grade 6 carbon per cc. solution. ● 0.00877 g. GR-S per cc. solution. ■ 0.0136 g. GR-S per cc. solution. ▲ 0.01904 g. GR-S per cc. solution.

rigidity of the rubber layer to maintain a spherical shape at low rates of shear. At the highest rates of shear the maximum possible deformation of the suspended spheres has been reached and correspondingly a lower constant viscosity. Figure 12 shows in schematic drawings an undeformed sphere, a slightly deformed one and, finally, one considerably deformed.

FIG. 12.—Rubber layer surrounding the carbon particle, showing: (a) the layer at zero rate of shear, (b) slightly deformed layer at intermediate rate of shear, (c) strongly deformed layer at highest rate of shear.

The thickness of the adsorbed layer of GR-S on the carbon black particle is of the order of 150 to 200 Ångstrom units, in agreement with electron microscopic examination.

There seems to be a definite trend in the values of the thickness of the rubber layer surrounding the particle and in the concentration of the rubber layer. The relative viscosities at zero rate of shear for any given carbon concentration decrease with increasing concentration of the rubber solution for the lower carbon concentrations and pass through a minimum for the higher ones. These phenomena undoubtedly are caused by the selectivity of the adsorption, perhaps as to the molecular weight of the rubber, and to the ratio of the rigidity of the rubber layer and the viscosity of the rubber solution.

Further experiments are underway to gain additional information on these points. Other carbon blacks, different molecular weight fractions of GR-S, and solutions of other elastomers are being investigated.

SUMMARY

The viscosity of carbon black suspended in GR-S solutions has been investigated in a Stormer-type viscometer at various rates of shear. Relative viscosities thus determined have been extrapolated to zero rate of shear and, by applying Einstein's viscosity equation, the volume of the suspended particles has been calculated. It has been found that, under the conditions examined, the carbon black particles are surrounded by a rubber layer 150 to 200 Ångstroms thick.

REFERENCES

[1] Rehner, *J. Applied Physics* **14**, 638 (1943).
[2] Smallwood, *J. Applied Physics* **15**, 758 (1944).
[3] Einstein, *Ann. Physik* **19**, 289 (1906).
[4] Guth and Gold, *Phys. Rev.* **53**, 322 (1938); see also Guth, *J. Applied Physics* **16**, 20 (1945).
[5] Goldfinger, RUBBER CHEM. & TECHNOL. **18**, 286 (1945); *J. Polymer Science* **1**, 58 (1946).
[6] Manufactured by I. Sorvall, Inc., New York.

NEW TYPES OF HIGHLY ELASTIC SUBSTANCES. VULCOLLANS *

O. BAYER, E. MÜLLER, S. PETERSEN, H. F. PIEPENBRINK AND E. WINDEMUTH

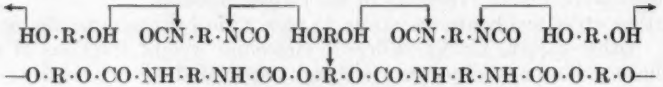
MAIN SCIENTIFIC LABORATORY, FARBENFABRIK BAYER, LEVERKUSEN, GERMANY

INTRODUCTION

The process of polyaddition of diisocyanates, which in principle is the addition of diisocyanates to dihydroxy and polyhydroxy compounds and to other compounds containing two or more reactive hydrogen atoms, makes it possible to synthesize products of high or even extremely high molecular weight, and with practically predetermined structures and properties, from small molecules.

In the present work, it is shown that, by means of the diisocyanate process, it is possible also to prepare new types of highly elastic and valuable products of the character of vulcanized rubber.

When diisocyanates are added to glycols, linear polymers (polyurethans) are obtained, and these can be spun into fibers and stretched (Perlon-U)[1].



Mechanism of polyurethan formation

If compounds which contain more than two hydroxyl groups are made to react with diisocyanates, high-molecular compounds having a network structure are obtained, as exemplified in Figure 1.

Industrially the particular polyhydroxy compounds which have found application are those which can be easily obtained by esterification of dibasic acids with an excess of bivalent and tervalent alcohols, e.g., Desmophene[2]. Here the general rule holds good that the higher the content of aromatic (phthalic acid) and trifunctional (glycerol) constituents, the harder and more friable are the transformation products and, conversely, the higher the content of aliphatic dicarboxylic acids and glycols, the softer and more elastic are the transformation products. As far back as 1941 it was shown that it is possible to obtain a highly elastic synthetic product by reaction of hexadiisocyanate with a polyester which is composed essentially of adipic acid and a mixture of 1,4-butanediol and trimethylolpropane.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Angewandte Chemie*, Vol. 62, No. 3, pages 57–66, February 7, 1950. This is the 6th Communication on the general subject of Polyurethans. (Part 1, Bayer, *Ann.* **549**, 286 (1941); Part 2, Bayer, *Angew. Chem.* **59**, 257 (1947); Part 3, Hebermehl, *Farben, Lacke, u. Anstrichstoffe* **8**, 123 (1948); Part 4, Siefken, *Ann.* **562**, 75 (1949); Part 5, Petersen, *Ann.* **562**, 205 (1949)). The work was commenced in 1943 in the Main Scientific Laboratory of the former I.G. Farbenindustrie A.G., Werk Leverkusen, and was carried out in coöperation with the Divisions of Applied Technology. Continuance of the work after the War met with great difficulties, and since meantime similar products have been prepared elsewhere with the aid of the principle of diisocyanate addition developed by the present authors, it was decided to publish a part of the scientific results obtained up to the present time while the investigation is still under way and when a point has been reached when methods of application must now be developed.

Hofman[3] was the first to prepare pure linear polyesters from dicarboxylic acids and glycols. Later these products were studied more thoroughly by Carothers[4] and by Fuller[5]. In contrast to polyamides and urethans, they have, with the exception of terylene[6], no practical significance, since as a rule they are oils or waxes with softening points in most cases below 100° C. In only a few cases has it been possible to carry the esterification far enough to obtain high molecular synthetic products which can be spun and stretched, *e.g.*, the polyester of glycol and sebacic acid[4].

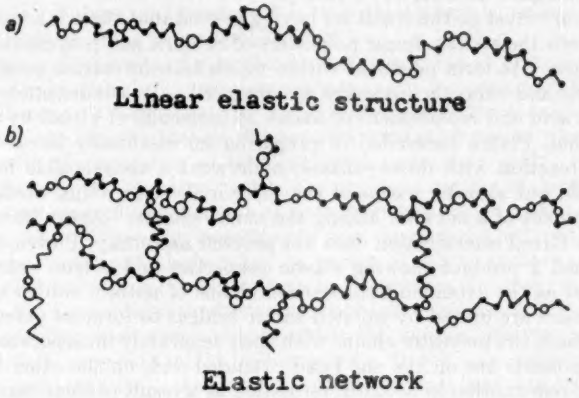


FIG. 1.

However, in view of the method of preparation, these linear polyesters must be bifunctional, and carry either hydroxyl groups or carboxyl groups. Isocyanate groups can react readily with both these groups. Polyesters are in most cases prepared by thermal esterification of the reagents, and, by the use of an excess of the dicarboxylic acid or of the glycol, carboxypolyesters and hydroxypolyesters are formed, *i.e.*, products which carry preponderantly terminal COOH or OH groups[7].

$$HO(CH_2)_2\cdot O\cdot OC(CH_2)_4CO\cdot[O\cdot(CH_2)_2\cdot O\cdot CH(CH_2)_4CO]_n\cdot O\cdot(CH_2)_2\cdot OH$$

Polyesters of ethylene glycol and adipic acid

In reality hydroxypolyesters of this type represent only a special type of high molecular glycols. In work in 1940 on the transformation of linear polyesters by diisocyanates, Schlack[8] undertook to increase greatly the chain length of these hydroxypolyesters. When such a polyester is treated with the exact equimolecular quantity of a diisocyanate, *e.g.*, with hexane-1,6-diisocyanate, there is an increase in the length of chain, and formation of what may be a mixed carbamic acid-carboxylic acid-polyester:

$$(x+1)(HO\overset{\text{Polyester}}{\text{———}}OH) + x(OCN(CH_2)_6NCO) \rightarrow$$

$$HO\overset{\text{Polyester}}{\text{———}}O[CO\cdot NH\cdot(CH_2)_6\cdot NH\cdot CO\cdot O\overset{\text{Polyester}}{\text{———}}O]_{x-1}$$

$$HO\overset{\text{Polyester}}{\text{———}}O\cdot CO\cdot NH(CH_2)_6\cdot HN\cdot CO$$

This transformation is in most cases carried out with the polyester in a fused state, and on addition of the diisocyanate the viscosity increases appreciably. The synthetic product obtained shows, when carefully prepared, the expected properties. The fusion mixture is stringy, and the products thus obtained can be stretched to several times their original lengths, as, for example, superpolyamides. Their technical value remains, however, rather limited, since in all cases they still have very low softening temperatures. However, Schlack observed at the time that, in some cases, elastic products also are formed, but he did not investigate the subject further[9].

To Pinten[10] must go the credit for having proved that there is a very narrow range between the strictly linear polyesters of Schlack and polyesters having a strong tendency to form networks within which transformation products with highly elastic and valuable properties are observed. By condensation of glycol with adipic acid and replacement of about 25 molecules of glycol by a trifunctional alcohol, Pinten succeeded in preparing an essentially linear polyester which, by reaction with diisocyanates, underwent a considerable increase in chain length, but also, by means of the three hydroxyl groups, made possible the development of a network among the macro-chains. Apart from the fact that such a mixed esterification does not proceed uniformly, Pinten, nevertheless, obtained a product showing elastic properties and a true vulcanization effect. Just as the extended hydrocarbon chains of natural rubber and butadiene polymers are united by isolated sulfur bridges to form an extensive network structure, the polyester chains with their separately incorporated trifunctional components are on the one hand extended and, on the other hand, are united with one another in network formation as a result of their reaction with the diisocyanate.

The products obtained by Pinten were named I rubbers (isocyanate rubbers). This new type of industrial material, which can be molded at high temperatures, showed certain noteworthy properties, *e.g.*, high tensile strength and resistance to abrasion, and only a slight damping effect[11]. The chief obstacles in the way of its practical use are its very poor resistance to tearing (or, in rubber parlance, its structure), and the highly undesirable property of changing in volume (elongating) and hardening when kept for a while at low temperatures.

Today it is known that loss of high elasticity is the result of the crystallization of the polyester constituent, and by warming or by mechanical stressing, this crystallization is destroyed, and the material regains its rubberlike elasticity[12].

As a result of an extended investigation of the reaction of linear polyesters with diisocyanates from the great number of possible reactions of polyhydroxy compounds with diisocyanates, certain noteworthy facts were established which led finally to the development of the highly elastic and valuable product which is now known as Vulcollan.

For various reasons the investigation was confined to strictly linear polyesters, and attention was directed to the problem of having the network develop, not within the polyester, but at its ends.

REACTION OF LINEAR POLYESTERS WITH VARIOUS POLYISOCYANATES

The polyester of ethyleneglycol and adipic acid, which carries terminal hydroxyl groups, was first studied. Products with terminal networks are natu-

rally formed directly when this polyester is treated with triisocyanates, but the resulting elastomers show only slight tear resistance.

Consequently the experiments were directed toward diisocyanates. Those containing nitro groups[13] were first tested, in particular 2-nitro-phenyl-4,4′-diisocyanate, with the idea that they might, by subsequent reduction of the nitro groups, form connecting azo or azoxy bridges. Actually highly elastic valuable synthetic products with heretofore unknown high tear resistance were obtained through the agency of these diisocyanates. However, the elastomers were formed under conditions which made the expected chain-linking reaction improbable. Subsequent treatment with reducing agents, such as sulfur and formaldehyde, resulted in no further effect.

The unique behavior of nitrodiisocyanate remained at first uncertain, particularly as the already known diisocyanates such as hexane-1,6-diisocyanate, 1-methylbenzene-2,4-diisocyanate, 1-chlorophenyl-2,4-diisocyanate, and diisocyanates of the biphenyl series, did not give promising results when they were treated with the polyester of ethyleneglycol and adipic acid. With strictly anhydrous polyester and the exact equimolecular quantity of diisocyanate, extended linear macromolecules such as were described earlier in the present paper were obtained. When the experiments were carried out without any special precautions, and particularly when an excess of diisocyanate was used, soft, viscous, blistered molded products were in many cases obtained: in a few cases, however, the final molded products were rubberlike and usable.

The question then arose as to whether the unique behavior of 2-nitro-diphenyl-4,4′-diisocyanate might be connected with the polar nitro group, which impedes free rotation. Accordingly other diphenylisocyanates with rigid structures were studied, *e.g.*, 2,7-diphenylsulfone diisocyanate. In this case too, the product obtained had excellent properties. This in turn led to the idea that it is not the polar group but, in general, a certain expanse of structure of the diisocyanate which is necessary for the resulting product to have good elastic properties. This working hypothesis proved to be a fortunate one, for diisocyanates which fulfilled this requirement, *e.g.*, the diisocyanates of pyrene, chrysene, and fluorene, gave elastic products of unquestioned value. Furthermore, diisocyanates of the naphthalene series, in particular naphthalene-1,5-diisocyanate[14], were found to be exceptionally adaptable to this synthesis[15].

Table 1 shows some results which were obtained with this same ester of ethyleneglycol and adipic acid with various diisocyanates.

These newly developed polycyclic diisocyanates with expansive structures are fixed like nodes at uniform distances in the extended linear polyester chain. It would appear that the alternation in the linear and structurally expansive constituents, together with the development of a network structure play an essential part in the remarkable plastic properties of these new synthetic products[16]. The aromatic constituents act as interposed elements or nodes in an otherwise linear structure[17].

For the moment it remains unexplained in what way purely linear polyesters and the newly developed structurally expansive isocyanates can form highly elastic synthetic products which show all indications of being composed of giant network molecules. Above all it remains for the present unexplained how an empirical excess of 40–50 per cent of diisocyanate is necessary to obtain good results. One is inclined to take the view for the time being that the extended polyester urethan molecules are strictly linear, and that their great chain length and their structurally expansive groups which oppose uncoiling would have an effect equivalent to the development of a chemical network. However, a

TABLE 1

REACTION PRODUCTS OF THE UNDRIED POLYESTER OF ETHYLENEGLYCOL AND ADIPIC ACID AND VARIOUS DIISOCYANATES (APPROXIMATELY 30 PER CENT IN EXCESS OF THE AMOUNTS CALCULATED ON THE BASIS OF HYDROXYL GROUPS)

Diisocyanate	Tensile strength (kg. per sq. cm.)	Elongation at rupture (%)	Structural strength* (kg. per sq. cm.)	Notes
Hexamethylene	—	—	—	worthless hardens at once
1-Methylbenzene-2,4-	(200–250)	(730)	(83)	mostly blistered difficultly reproducible high permanent set
2-Nitrodiphenyl-4,4′	188	743	122	—
2-Nitrodiphenylmethane-4,4′-	197	629	75	—
Diphenylmethanesulfone-4,4′-	240	736	108	—
Diphenylsulfone-4,4′-	215	331	138	—
Naphthalene-1,4-	315	756	134	—
Naphthalene-1,5-	311	765	167	—
Naphthalene-2,7-	402	758	163	—
Fluorene	435	660	142	—
Chrysene	300	684	133	—

* The structural strength here and as shown in the subsequent tables was measured with 4-mm. test-specimens (rings with 1-mm. notches) and calculated to a basis of kg. per sq. cm.

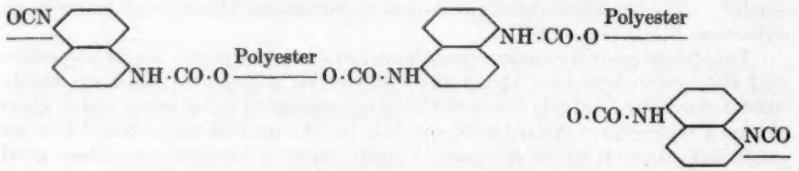
simple calculation shows that, with the excess of diisocyanate necessary for good results, no long chains can be formed[18] unless further secondary reactions are assumed.

THE MECHANISM OF NETWORK FORMATION

A more thorough study showed that in many cases the experiments were not reproducible, particularly with large amounts of reagents. As an explanation, it was soon discovered that the ester of glycol and adipic acid is hygroscopic and that a moisture content of about 0.1 per cent is the optimum content necessary for the synthesis of rubberlike products.

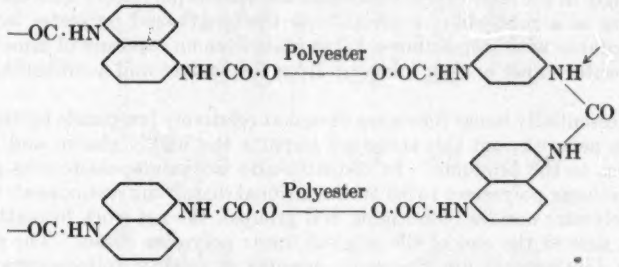
In this way only was the decisive role of moisture in the mechanism of the reaction realized, and this led the present authors later, after a long series of experiments, to a better understanding of the structure of these new highly elastic products on the basis of linear polyesters[19].

The results can be briefly summarized thus. Without water, the only reaction which the diisocyanate undergoes is an increase in chain length; otherwise it must be assumed, in view of its being in excess, that chains with terminal isocyanate groups are formed, perhaps of the general composition:



With 30 per cent excess of diisocyanate above the amount corresponding to the hydroxyl number of the polyester, only 2 to 3 polyester molecules actually are linked to one another. Such products are present in the anhydrous fusion

mixture, and they do not change significantly even on being heated longer. If water is then added, the isocyanate groups which are underlined in the scheme above as terminal groups on the chains react, just as do all isocyanate groups, with formation of urea bridges. At the same time, carbon dioxide is liberated in an amount which volumetric analysis shows to be the theoretical value, and any free isocyanate groups still present disappear, as can be shown likewise analytically. Schematically the new structure might well be of the following character:



Urea bridges alternate with carbamic acid ester and carboxylic acid ester groups. The chain is thereby extended still further, but it still retains its general linear structure. The newly formed urea bridges, however, introduce a wholly new feature in the scheme, for they contain reactive hydrogen atoms which in their turn are in a position to react with isocyanates. This is probably the necessary condition for the formation of bridges. Furthermore, low-molecular bilaterally substituted urea derivatives are already known to react with isocyanates, with displacement of hydrogen in the following way:

$$—NH·CO·NH— + RNCO \rightarrow —N(CO·NHR)·CO·NH—$$

In the case of polyesters containing isocyanate groups, however, this reaction leads to network formation, and this in turn to 3-dimensional giant molecules.

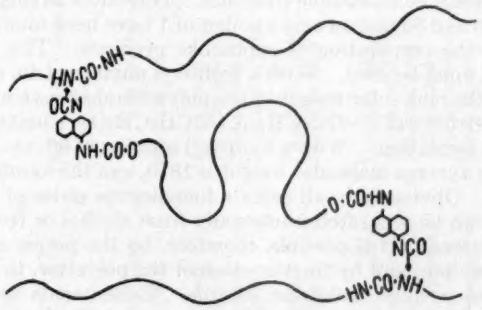


FIG. 2.

On this basis, the synthesis of these new highly elastic products involves three steps, which will be considered in detail:

(1) Preparation of the linear polyester;
(2) Increase in chain length, with formation of the polyester isocyanate;
(3) Formation of urea with water, and development of a network[19].

It is of advantage in the preparation and processing of Vulcollan to carry out steps (2) and (3) separately and successively. If the polyester contains water, as was true in the first experiments, the lengthening of the chains, formation of urea, and development of a network proceed under confused conditions; accordingly in the later experiments only anhydrous polyesters were used. The formation of a rubberlike material from the lengthened polyester isocyanate (in accordance with step 3 above) takes place even on exposure of films to moist air, for water vapor is then taken up from the surface and a rubberlike skin is formed.

The essentially linear forms are united at relatively few points by the formation of a network, but this structure imparts the highly elastic and valuable properties to the products. In distinction to isocyanate elastomers prepared from nonlinear polyesters (with tridimensional disturbing components) or from linear polyester amides (containing NH groups), the net work formation takes place at first at the end of the original linear polyester chain. The points of network development are, therefore, oriented in a fairly uniform arrangement and relatively far apart, and this may explain the superior properties of the new polyester elastomers.

PREPARATION OF LINEAR POLYESTERS

Linear polyesters as starting materials for Vulcollan will first of all be discussed. The simple glycol-adipic acid polyester with hydroxyl number of 50–60 represents the ideal starting material as far as physical properties, particularly structural strength, and technical availability, are concerned.

Esterification is carried out either by heating the components together, or by first fusing the adipic acid and then adding the glycol extremely slowly. In 20 to 40 hours the water is distilled off at a gradually rising temperature (160–220° C), and the esterification is completed by subsequent heating in a vacuum[21].

Before its reaction with a diisocyanate, the ethyleneglycol-adipic acid polyester is a hard wax, with softening range of 60–70° C. Roentgenographic examination reveals no crystalline structure. Polyesters having hydroxyl numbers between 40 and 60 and an acid number of 1 have been found to be particularly suited to the preparation of rubberlike products. This means that an excess of glycol must be used. With a hydroxyl number of 40, *i.e.*, 1.2 per cent of OH groups, the molecular weight of the polyester chain averages about 2800, *i.e.*, about 16 structural ($—OC(CH_2)_4COOCH_2CH_2O—$) units are linked together in chain formation. With a hydroxyl number of 60, *i.e.*, 1.8 per cent of OH groups, the average molecular weight is 1870, and the number of structural units is 10–11. Obviously in all cases a homologous series of polymers is involved, which can be separated fractionally from alcohol or from a mixture of alcohol and benzene. It is possible, therefore, by the proper choice of conditions for the reaction, and by fractionation of the polyester, to synthesize products of various average molecular weights. Experiments to determine the influence of the length of chain on the properties of the final product are described later in the section on "Elongation". It must, however, be pointed out that all samples of Vulcollan prepared from ethyleneglycol-adipic acid polyesters have shown a certain tendency to harden during storage for long periods.

TABLE 2

REACTION PRODUCTS OF SIMPLE POLYESTERS WITH NAPHTHYLENE-1,5-DIISOCYANATE

Glycol constituent	Acid constituent	Consistency	Tensile strength (kg. per sq. cm.)	Extensibility (%)	Structural strength (kg. per sq. cm.)	Remarks
Ethyleneglycol	Succinic acid	Solid wax	273	625	120	High permanent set; hardens and becomes leathery
Ethyleneglycol	Adipic acid	Solid wax	350	640	158	Slowly hardens
Ethyleneglycol	Pimelic acid	Liquid	—	—	—	—
Ethyleneglycol	Sebacic acid	Solid wax	—	—	—	Hardens immediately on cooling; only highly elastic at elevated temperatures
Ethyleneglycol	Decamethylene dicarboxylic acid	Solid wax	—	—	—	
Ethyleneglycol	Diglycolic acid	Resin	270	570	147	Leathery; very easily saponified
Ethyleneglycol	Phthalic acid	Brittle resin	107*	261*	87	*Processible only with 25% of dibutyl phthalate; glasshard without softener
1,2-Propyleneglycol	Succinic acid	Liquid	180	670	96	Leathery; highly elastic at 70° C
1,2-Propyleneglycol	Adipic acid	Liquid	220	780	92	Does not harden
1,2-Propyleneglycol	Phthalic acid	Brittle resin	—	—	—	—
2,3-Butyleneglycol	Adipic acid	Liquid	179	630	92	Does not harden
1,6-Hexanediol	Adipic acid	Solid wax	248	610	122	Hardens
Hexahydroresorcinol	Succinic acid	Resin	113	223	82	Leathery

VARIATIONS IN THE POLYESTER

There is, of course, a wide range of polyesters, so extensive experiments were carried out to find materials which would not show the disadvantageous tendency to harden and to become crystalline[22]. There were, in principle, two possibilities. On the one hand it was possible to work with individual polyesters prepared from other components, *i.e.*, with polyesters prepared from one glycol and one dicarboxylic acid. Some of the results which were obtained with such pure and simple polyesters are summarized in Table 2. On the other hand it is possible to synthesize linear polyesters from more than two components. These are designated in general as mixed esters. The possible combinations with mixed esters are great, both with respect to the number of the condensed constituents and also to the proportions of the original reagents; but only a relatively few representative combinations could be studied, as shown in Table 3. This table contains only mixed esters in which the system: ethyleneglycol-adipic acid polyester, was extended by a third bifunctional constituent.

In all experiments in this range of polyesters, the mechanical properties of the products were determined, and special attention was paid to the hardening of the products. As is evident in the tables, in no case were the mechanical properties of the ethyleneglycol-adipic acid polyester surpassed. On the other hand it was found possible to synthesize a series of polyesters which had far less tendency to harden.

With respect to any relationship between the physical properties of the polyesters and the tendency of the final Vulcollan products to harden, polyesters with high melting points give, as a general rule, products which tend to harden, whereas polyesters which are either liquid at room temperature or fuse at only moderately high temperatures give Vulcollan products which do not lose their high elasticity, even on long storage[23]. Typical of the types of Vulcollan esters which have a strong tendency to harden are, for example, the ethyleneglycol-sebacic acid polyester and the ethyleneglycol-succinic acid polyester, which in general have less desirable properties than those of the ethyleneglycol-adipic acid polyester. These condensates become highly elastic only at relatively high temperatures. The introduction of expansive constituents into these polyesters does relatively little good in general (see, for example, the ethyleneglycol-phthalic acid polyester), because the tendency to harden is increased. Moreover, unsaturated constituents, such as butenediol, butinediol, and maleic acid, are of no particular advantage[24]. Tables 3 and 4 show, in addition, that the introduction of unsaturated and sulfur-bearing constituents leads in some cases to difficulties in esterification.

From the great number of experiments which were carried out, and only a few of which have been selected for presentation in the present work, it is evident that 1,2-propyleneglycol is of special value as a constituent of the ester. The pure ester of 1,2-propyleneglycol and adipic acid is a liquid at room temperature, and it gives a Vulcollan which does not harden. Of course the mechanical properties of the products formed with naphthylene-1,5-diisocyanate are poorer than those of the corresponding ethyleneglycol ester.

In the case of the mixed esters from these two glycols, the loss in quality is not so noticeable. About 30 per cent of 1,2-propyleneglycol is sufficient to prevent practically any hardening of the final product. Experiments were also carried out to determine whether a mixture of ethyleneglycol-adipic acid polyester and 1,2-propyleneglycol-adipic acid polyester could be used instead of a mixed ester of the three components, *i.e.*, adipic acid on the one hand and ethyl-

TABLE 3

REACTION PRODUCTS OF MIXED ESTERS WITH NAPHTHALENE-1,5-DIISOCYANATE

Irregular component	Mole ratio based on 100 moles adipic acid	Consistency	Tensile strength (kg. per sq. cm.)	Extensibility (%)	Structural strength (kg. per sq. cm.)	Hardening
1,2-Propyleneglycol	100:15	Solid wax, low m.p.	221	810	158	(+)
1,2-Propyleneglycol	100:20	Solid wax, low m.p.	272	745	122	–
1,3-Butyleneglycol	100:15	Solid wax, low m.p.	146	650	84	(+)
Diethyleneglycol	100:15	Solid wax, low m.p.	180	720	79	–
Glycerol-α-monomethyl ether	100:15	Solid wax, low m.p.	165	525	92	–
Thiodiglycol	100:15	Solid wax, low m.p.	–	–	–	–
Buteneglycol	100:14	Solid wax, low m.p.	306	680	86	(+)
Buteneglycol	100:33	Solid wax, low m.p.	254	650	54	–
Butine glycol	100:20	Solid wax, low m.p.	Easily cracked tarry product			
Hydroxyethylaniline	100:10	Solid wax, low m.p.	222	660	87	+
Hydroxyethylaniline	100:6	Solid wax, low m.p.	266	630	108	++
Hydroxyethylaniline	100:3	Solid wax, low m.p.	259	700	165	++
Dihydroxyethylaniline	100:15	Solid wax, low m.p.	155	680	67	(+)
β-Dihydroxyethylnaphthylamine	100:10	Solid wax, low m.p.	230	675	92	(+)
Piperazine	100:3	Solid wax, low m.p.	151	645	95	(+)
Piperazine	100:2.2	Solid wax, low m.p.	344	720	112	+
Piperazine	100:2.1	Solid wax, low m.p.	367	820	133	+
Succinic acid	100:100	Liquid	130	590	33	–
Sebacic acid	100:100	Solid wax	–	–	–	–
Methyladipic acid	100:20	Solid wax, low m.p.	143	610	75	–
Thiodipropionic acid	100:15	Solid wax	–	–	–	++
Maleic acid	100:33	Swollen	–	–	–	–
Phthalic acid	100:35	Brittle resin	202	463	118	++

The mixed esters were mostly prepared from ethyleneglycol and adipic acid, and contain as a third component the components shown in this table.

TABLE 4

MIXED ESTERS AND MIXTURES OF ESTERS

Reagents	Tensile strength (kg. per sq. cm.)	Extensibility (%)	Permanent set (%)	Structural strength (kg. per sq. cm.)	Hardness (Shore)	Elasticity	Hardening
Simple ethyleneglycol-adipic acid polyester	350	640	6	158	60	69	++
Mixed ester of ethyleneglycol, 1,2-propyleneglycol and adipic acid	283	725	15	133	65	65	(+)*
Mixture of esters: 70 parts glycol-adipic acid ester and 30 parts 1,2-propyleneglycol-adipic acid ester	300	730	13	145	67	63	(+)*
Mixed ester of ethyleneglycol, 1,2-propyleneglycol (50:50) and adipic acid	270	700	20	108	71	70	—
Mixture of esters: 50 parts ethyleneglycol-adipic acid ester and 50 parts 1,2-propyleneglycol-adipic acid ester	250	680	14	117	66	70	—
Simple 1,2-propyleneglycol-adipic acid ester	220	780	14	92	69	76	—

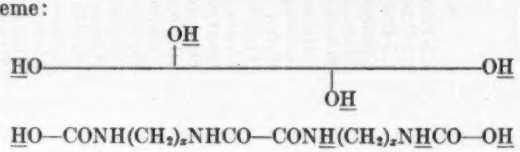
* Only in the stretched state[7].

eneglycol and 1,2-propyleneglycol on the other[25]. Table 4 shows that, whichever method of synthesis is used, the decline in mechanical properties is almost directly proportional to the increase in the 1,2-propyleneglycol content. From the standpoint of actual manufacture, therefore, the two types of simple esters can be used, and they can be mixed at will before carrying out the condensation reaction. The content of 1,2-propyleneglycol ester is governed by what is required with respect to ultimate hardening of the Vulcollan.

The investigation of the various polyesters was further complicated by the fact that each polyester had to be studied with so many different diisocyanates (Tables 2, 3, and 4 show the results only with naphthylene-1,5-diisocyanate). Actually polyesters were found later which, in contrast to the simple ethyleneglycol-adipic acid polyester, also gave useful products with diisocyanates, such as hexamethylene diisocyanate and 1-methylbenzene-2,4-diisocyanate.

Better results are obtained by the reaction of 1,2-propyleneglycol-adipic acid ester with hexamethylene diisocyanate, as evidenced by the product having a tensile strength of 235 kg. per sq. cm., and extensibility of 1000 per cent, and a structural strength of 58 kg. per sq. cm. This high elongation is of advantage; on the other hand, the structural strength is too low.

With regard to the reaction with simple aliphatic diisocyanates, socalled amide polyesters represent a special case. Amino alcohols and diamines can be introduced into these polyesters as irregularly fixed constituents, *e.g.*, ethanolamine, hexanolamine, ethylenediamine, butylenediamine, and hexamethylenediamine. The products, which contain a primary amine group, give linear ester amides. Nevertheless they contain in the chain amide groups, —NHCO—, the hydrogen atom of which can take part in the reaction with diisocyanates. Amido esters of this type are, therefore, analogous rather to the type of ester used in the synthesis of Troisdorfer isocyanate elastomers, as shown by the following scheme:



HO—CONH$(CH_2)_x$NHCO—CONH$(CH_2)_x$NHCO—OH

The hydrogen atoms which are underlined are reactive with diisocyanates.

This type of polyester amide gives with various diisocyanates highly elastic and useful synthetic products. Since, however, these products are a departure from the strictly linear form, the maximum values can hardly be expected to be atained. But such types of products might find use as adhesives or as coating materials[26]. The ester elastomer Vulcaprene is based in part on this type.

If secondary amine groups are introduced into the polyester chain, the hydrogen atoms in the chain lose their reactivity. Experiments with hydroxyethylaniline and piperazine as irregular constituents in the reaction with naphthylene-1,5-diisocyanate are shown in Table 3.

A particularly suitable secondary diamine is piperazine, which has already been used as a constituent of linear polymers[27]. Ethyleneglycol-adipic acid esters containing piperazine give with excess hexamethylene diisocyanate very valuable elastic products, the mechanism of network formation of which (with water or moisture) is explained in exactly the same way as described above. A polyester containing 15 mole-per cent of piperazine showed[19] a tensile strength of 280 kg. per sq. cm., extensibility of 790 per cent, structural strength of 125 kg. per sq. cm., and hardness (Shore) of 68. These values approach those of the product formed from ethyleneglycol-adipic acid ester and naphthylene-1,5-diisocyanate, but, unlike the latter product, there is no discoloration on exposure to light. Naturally here too there is a tendency to harden. From the practical viewpoint, the product formed by this particular combination of raw materials is out of the question because of the high price of piperazine.

In any case the present work shows that combinations of polyesters and diisocyanates must still be formulated without any satisfactory knowledge at this time[16] regarding the influence of such factors as irregularity of structure, possibility of crystallization, reactivity, secondary reactions of the diisocyanate, etc., on the final product.

It should be emphasized, however, that the ethyleneglycol-adipic acid polyester and the 1,2-propyleneglycol-adipic acid polyester in combination with naphthylene-1,5-diisocyanate are likely to become outstanding in the field of synthetic products, and at present are represented by Vulcollan.

CHAIN LENGTHENING

As already pointed out, a linear polyester can be made to react with diisocyanates without any network formation only if every trace of moisture is excluded. It is always advantageous first to prepare the socalled extended isocyanate polyester, *i.e.*, to stop the reaction at this stage, and to carry out the reaction involving network formation only as a subsequent process. In the first experiments in the present work, as summarized in Tables 1 to 3, this was not taken into consideration. Later however, the polyester was always dried before being allowed to react with the diisocyanate.

Dehydration was effected by fusion in a vacuum at about 120° C, and either passing an inert gas through the system or employing a drying agent. Another possible way, in case it is desired to work with a solvent, is azeotropic distillation. Finally chemical dehydration is possible, *e.g.*, by the addition of calcium carbide.

The reaction with the diisocyanate, which is usually carried out at 100–130° C, is exothermic. Since the amount of diisocyanate is in excess of the calculated proportion, the chain growth and consequent observed increase in viscosity are not very marked. The desired transformation is complete in a

few minutes; however, the reaction mixture can be heated for several hours longer without any noticeable change. On extremely long heating, the mixture containing the highly reactive naphthylene-1,5-diisocyanate has a tendency to gel because the elongated isocyanate polyester molecule contains a few urethan hydrogen atoms, which, although extraordinarily inactive, or at least far slower to react than the hydrogen atoms of the urea bridges, can and do react with isocyanates[28].

To throw light on the influence of the hydroxyl number of the polyester and the optimum proportion of isocyanate in the simple system: ethyleneglycol-adipic acid polyester + naphthylene-1,5-diisocyanate, numerous experiments, some of which are shown in Tables 5 and 6, were carried out. Table 5 shows

TABLE 5

ETHYLENEGLYCOL–ADIPIC ACID ESTERS OF DIFFERENT HYDROXYL NUMBERS EXTENDED WITH NAPHTHYLENE–1,5,-DIISOCYANATE TO A MOLECULAR WEIGHT OF 4000

Polyester		Isocyanate (g. per 100 g. polyester)	Mol. wt. after extension	Tensile strength (kg. per sq. cm.)	Extensibility (%)	Stress at 300% elongation (kg.)	Structural strength (kg. per sq. cm.)	Elasticity	Hardness (Shore)	Hardening
OH no.	Mol. wt.									
49*	2290	15.2	4000	392	680	94	192	58	65/71	↓
32	3500	11.9	4000	348	560	131	250	65	67/73	
36	3100	12.6	4000	305	610	111	172	59	68/73	decreasing tendency
46	2440	14.6	4000	351	645	113	186	59	71/76	
54	2080	16.2	4000	385	635	130	185	60	71/76	
81	1385	21.6	4000	371	645	110	125	50	74/77	↓

* Unfractionated ester.

fractionated polyesters, having various hydroxyl numbers, which were made to react with enough naphthylene-1,5-diisocyanate for the elongated product to have an average molecular weight of about 4000. Under these conditions the ester with the smallest hydroxyl number gave the best mechanical properties; however, at the same time the product showed the greatest tendency to harden. Table 6 records a series of experiments in which the fractionated polyesters with various hydroxyl numbers were in every case extended by sufficient naphthylene-1,5-diisocyanate for the calculated molecular weight to increase about 1.8 or 1.9-fold. The products show almost the same tensile strengths and structural strengths, with higher hydroxyl numbers, *i.e.*, lower molecular weight of the polyester, the hardness and the modulus (measured in kg. per sq. cm. at an elongation of 300 per cent) are definitely higher. From these experiments and from other similar ones, it was possible to determine the most favorable conditions with respect to chain length of the polyester and the amount of excess isocyanate to be used. From a practical viewpoint, polyesters having hydroxyl numbers of 50 to 60 and an excess of isocyanate in the range of 40–60 per cent are used.

FORMATION OF UREA WITH WATER AND THE DEVELOPMENT OF A NETWORK STRUCTURE

The final stage involves the formation of a network structure by the extended isocyanate polyester through the agency of water. This can be effected in various ways. For example, steam can be passed through the viscous mass of isocyanate polyester at a temperature above 100° C until the mass becomes progressively more viscous and finally becomes a brittle solid. This process is best carried out on a large scale in a kneading machine. When the network de-

TABLE 6

ETHYLENEGLYCOL–ADIPIC ACID ESTERS OF DIFFERENT HYDROXYL NUMBERS EXTENDED WITH NAPHTHYLENE–1,5–DIISOCYANATE TO ABOUT 1.9 INCREASE IN MOLECULAR WEIGHT

Polyester		Isocyanate (g. per 100 g. polyester)	Mol. wt. after extension	Factor $\frac{\text{Extended mol. wt.}}{\text{Mol. wt. polyester}}$	Tensile strength (kg. per sq. cm.)	Extensibility (%)	Structural strength (kg. per sq. cm.)	Elasticity	Hardness	Stress at 300% elongation (kg.)	Hardening
OH no.	Mol. wt.										
24	4680	7.0	8920	1.90	390	770	158	—	59/63	55	↑
32	3500	9.5	6600	1.89	352	710	158	70	64/70	73	decreasing tendency
42	2670	12.5	5090	1.91	380	720	163	61	71/76	98	
52	2160	16.0	3885	1.80	322	726	150	60	71/86	119	
95	1180	30.5	2170	1.84	331	455	84	63	83/83	160	↓

velopment has reached the desired stage, the mass is ejected by the blades of the machine. It is still simpler to add water very gradually. The reaction follows the same course, and the amount of water can be controlled better (0.4–1.4 grams per 100 grams of mixture). It is important that the friable product obtained is in a condition to be milled out into a coherent sheet on a friction roll mill. This operation is common practice in the rubber industry. The sheet from the mill can be stored for some time, and under favorable conditions for days before it is molded. However, there is no doubt that even at room temperature it undergoes slow changes. A few hours' storage before molding appears to be advantageous. The sheet can be molded, *e.g.*, under a pressure of 50 to 200 kg. per sq. cm. for 10 to 15 minutes at 150–170° C. The molded products, *e.g.*, slabs, shoe soles, heels, packing, etc., are pale yellow to brownish when the Vulcollan contains no filler. The aromatic isocyanate imparts to the products a certain fluorescence, and also makes the products discolor and ultimately turn dark brown on exposure to light; but this is of no importance in the case of industrial products and of products containing fillers such as carbon black.

During molding, the reaction in the material continues to completion, *i.e.*, the last of the isocyanate groups which are still present disappear, and the final product develops its network structure. Account should also be taken of the fact that, under the influence of the pressure and temperature in the sense of the cleavage equilibrium described elsewhere by Petersen[29], isocyanate compounds may be released, and then reunited.

SOFTENERS AND FILLERS

A few remarks may not be out of place at this point concerning the behavior of Vulcollan when softeners and fillers are added. In itself it must be regarded as an advantage of this new synthetic product that, in contrast to the Buna type of elastomer, it is a highly elastic and valuable material even when no accessory ingredient has been added to it. Softeners and fillers can be added at various stages of the operations, either to the polyester before addition of isocyanate, or to the elongated isocyanate polyester, or, finally, to the material on the mill after network development is complete. This last method has been found to be the least desirable. Numerous softeners are compatible with the new products, *e.g.*, diethyl phthalate, hydroxycresyl comphane, derivatives of fat acids, ethyl thiobutyrate, Buna-32, aromatic sulfamides, and various others.

Even small additions of these softeners seem at first to have a pronounced softening effect on the material, but actually they tend to accelerate rather than to retard the ultimate hardening. Consequently, no further consideration was given to these softening agents.

It was quite otherwise with fillers. Here, as with natural rubber and Buna elastomers, a distinction must be made between "inactive" and "active" fillers. Inactive fillers, *e.g.*, barytes, talc, whiting, wood flour, etc., behave simply as diluents, and do not improve the mechanical properties in any way. On the contrary, there are other fillers which are known to be active in natural rubber, *e.g.*, active blacks and Calcil (calcium silicate), which, even in small percentages, likewise improve greatly the quality of Vulcollan. Table 7 shows data on the effects on the final reaction products of ethylene-glycol-adipic acid ester and naphthylene-1,5-diisocyanate and of 1,2-propylene-glycol-adipic acid ester and naphthylene-1,5-diisocyanate of adding different proportions of an active carbon black. The activity of this filler in the new Vulcollan products is evident in a progressive increase in the modulus and an increase in the hardness

TABLE 7

MEASUREMENTS OF THE PHYSICAL PROPERTIES OF TWO TYPES OF VULCOLLAN WITH INCREASING LOADINGS OF ACTIVE CARBON BLACK

Product	Carbon black (%)*	Tensile strength (kg. per sq. cm.)	Extensibility (%)	Permanent set (%)	Stress at 300% elongation (kg. per sq. cm.)	Hardness (Shore)	Structural strength (kg. per sq. cm.)
A	—	230	675	17	66	65	146
A	5	220	590	14	75	67	163
A	10	260	603	17	96	70	137
A	15	272	680	16	109	70	275
A	25	275	573	19	146	74	278
A	35	218	440	28	190	82	220
B	—	201	693	14	62	66	77
B	10	224	534	13	124	67	90
B	20	248	528	17	142	75	129
B	30	234	478	12	177	79	162

A—Vulcollan prepared from ethyleneglycol-adipic acid ester and naphthylene-1,5-diisocyanate.
B—Vulcollan prepared from 1,2-propyleneglycol-adipic acid ester and naphthylene-1,5-diisocyanate.
The carbon black was added to the elongated isocyanate polyesters, and the network development in the products was then effected by water.

* The carbon black content is expressed in percentages by weight based on 100 parts of polyester. The carbon black used was CK-III black.

as the percentage of carbon black is increased. Likewise increases in the structural strength and in the resistance to tearing are evident, which with increase in carbon black approach the tensile strength values (see also Figure 4).

Synthetic materials with such high resistance to tearing have not been known heretofore. Even the poorer 1,2-propyleneglycol ester product is remarkably improved by carbon black. The inherently low capacity of Vulcollan for being loaded with a filler can be increased by adding a softener along with the filler, and products having satisfactory mechanical properties for flooring and similar uses can then be made.

PROCESSING

Let us now consider the processing of Vulcollan from solution. It has already been pointed out that the extended isocyanate polyester is readily soluble in solvents such as methylene chloride, acetone, benzene, toluene, etc. These solutions can be used for the preparation of films by pouring, for the preparation of dipped goods, and for adhesives and coatings[30]. If moisture is excluded, these solutions are stable for some time. Products from inactive isocyanates have been developed which keep outstandingly well on storage.

Thin layers or films of the solution of Vulcollan soon lose their solvent by evaporation, and at the same time absorb water vapor from the air; in fact, enough water may be absorbed for films to pass through a series of intermediate stages to a final complete conversion to a highly elastic state. This reaction can be completed by heating. In any case the reaction requires a considerable time, *i.e.*, at the least several hours.

The problem then arose whether it might be possible to accelerate the formation of an isocyanate network. It had been known for a long time that pyridine can be used as a catalyst in isocyanate reactions. Basic catalysts were soon found which had a much more rapid action, and in amounts of 0.1 per cent or less had an accelerating action on the terminal network formation.

With all isocyanates the action of these catalysts depends on their accelerating the reaction with water. With highly reactive aromatic isocyanates there

TABLE 8

COMPARISON OF THE MOST ESSENTIAL PROPERTIES OF NATURAL RUBBER, BUNA, AND VULCOLLAN

Properties	Natural rubber		Buna-S		Vulcollan (A) from ethyleneglycol-adipic acid ester		Vulcollan (B) from propyleneglycol-adipic acid ester		Vulcollan (unloaded mixture of 70 parts A and 30 parts B)
	15 vol.-% carbon black	Unloaded	30 vol.-% carbon black	Unloaded	10 vol.-% carbon black	Unloaded	15 vol.-% carbon black	Unloaded	
Tensile strength (kg. per sq. cm.)	250	170	230	60	275	350	250	220	285
Extensibility (%)	500	700	500	500	550	650	480	750	725
Stress at 300% elongation (kg. per sq. cm.)	70	35	70	30	150	70	175	62	67
Hardness (Shore)	60	40	65	50	75	65	78	65	65
Structural strength (kg. per sq. cm.)	165	105	80	30	270	158	162	92	133
Elasticity (20° C)	35	70	50	65	50	65	52	76	65
Elasticity (70° C)	60	75	55	70	50	70	—	—	—
Resistance to benzine	200%	bad	10	14	3	3	—	—	—
Resistance to aromatic solvent	—	—	—	—	40	40	—	—	—
Alkali-acid resistance	++	++	++	++	−	—	—	—	—
Deterioration	+	+	++	++	+++	+++	+++	+++	+++
Resistance to ozone	−	−	−(+)	−(+)	+++	+++	+++	+++	+++
Resistance to heat	+	+	++	++	+−	+−	+−	+−	+−
Resistance to abrasion	100	>200	80	>200	45	30	—	—	—
Permeability to gases	1	—	1	—	—	0.1	—	—	0.05
Specific gravity	1.13	0.95	1.30	0.96	1.32	1.35	1.34	1.25	1.25

is the possibility of dimerization and trimerization reactions as well, as has been found to be true of diisocyanates[31]. In fact polymeric products separate out after only a short time from solutions of naphthylene-1,5-diisocyanate containing small amounts of such catalysts.

If these catalysts are used in not too great proportions, the mechanical properties of the final products are almost unaltered. Since here too the final effect is a synthetic product with a network structure, the product is insoluble, or at the most only swells, in organic solvents.

It is possible, therefore, to form thin walled articles by the molding process or pouring process from Vulcollan whose network structure has been developed by water. Molding to form thick sheets is impracticable because the development of a network structure in the isocyanate polyester involves the liberation of carbon dioxide. As a result, every solid molded article is necessarily blistered. This was originally a disadvantage of such products over isocyanate elastomers, which, thanks to their different mechanism of network formation, behaves satisfactorily in molding processes, *e.g.*, in centrifugal casting[32]. However, by proper modification of the network reaction, *i.e.*, the last stage of the synthesis, even Vulcollan with its superior mechanical properties can be successfully molded or cast. This development, which is so essential to the practical application of Vulcollan, will be described later.

PROPERTIES OF VULCOLLAN

It has been shown that Vulcollan products represent a new and valuable group of highly elastic materials. Table 8 shows a comparison of Vulcollan products prepared from various polyesters with loaded and unloaded natural rubber and Buna-S. This comparison of the different properties of Vulcollan

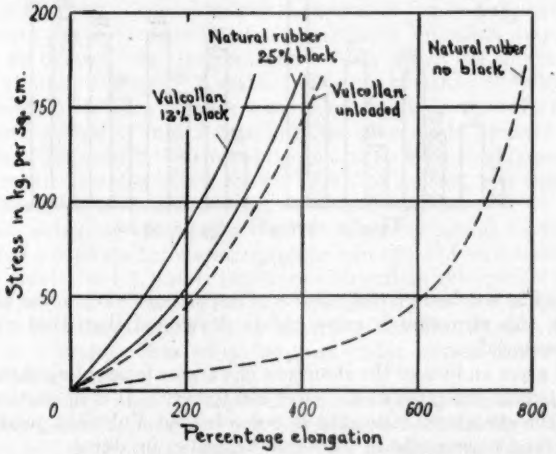


FIG 3.—Comparative stress-strain curves.

makes it evident that it cannot replace these older elastomers, as would hardly be expected in view of its totally different chemical structure, but it does represent a new type of synthetic material which is destined to win an important place among already known materials.

Its resistance to tearing and extensibility do not give clear evidence of its distinctive properties. Vulcollan products of the highest quality are particularly outstanding when not loaded, and, in complete contrast to natural rubber and Buna-S, they have, when loaded with carbon black, a tendency to show lower tear resistance.

The stress modulus at 300 per cent elongation and the hardness of Vulcollan are high. Figure 3 shows the stress-strain curves of Vulcollan in comparison with stress-strain curves of natural rubber. Unloaded Vulcollan shows approximately the same stress-strain curve as natural rubber containing carbon black.

Vulcollan represents, therefore, a stiff material which shows great resistance to reversible mechanical deformation. This characteristic is a drawback in some finished products, but is an advantage in the carcass of tires, in transmission belting, etc. The structure (resistance to the initiation and propagation

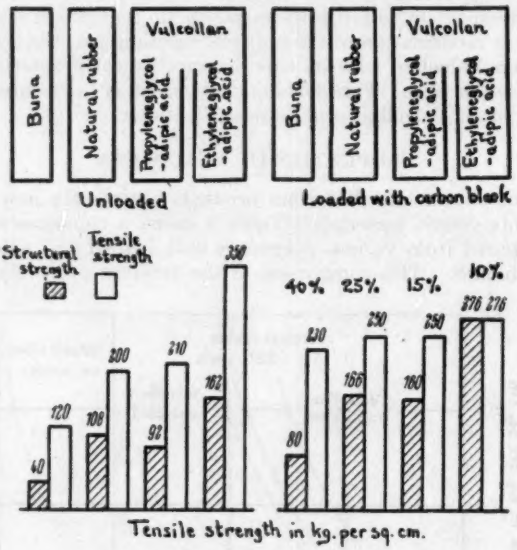


FIG. 4.

of tearing and to notched tearing) also is of importance and, as has already been pointed out, this structure is more highly developed than that of any other rubberlike material.

Figure 4 gives an idea of the structure of various types of elastomers in relation to the tensile strengths of the same elastomers. It is of particular significance that the structural strengths of some loaded Vulcollan products are as high as the tensile strengths of the same Vulcollan products.

The resistance to swelling in benzine and even in aromatic hydrocarbons is noteworthy, *e.g.*, only about 40 per cent in benzene. Benzene, acetone, and methylene chloride have the greatest swelling action. With increase in swelling, the strength decreases, but on subsequent shrinkage, the strength again attains its high value, as has been described for already known types of elastomers[33]. In contrast to this good resistance to swelling, is the very poor resist-

ance to acids and alkalies, which likewise is dependent on the polyester structure. By the prolonged action of boiling water, Vulcollan is decomposed through saponification, whereas it is extremely resistant up to 70° C. In boiling 15 per cent aqueous sodium hydroxide, Vulcollan is decomposed into its constituent parts in about 12 hours, and naphthylene-1,5-diamine, adipic acid, and glycol are recovered. This tendency to saponify must always be taken into account in any application of Vulcollan. The aging of Vulcollan is outstandingly good, and the sensitivity to oxidation inherent in unsaturated butadiene polymers is completely lacking. Likewise the resistance to ozone is noteworthy. On the other hand the resistance to heat is relatively poor. Up to 140° C the mechanical properties do not fall off to any greater extent than do those of Buna and natural rubber (see Table 9).

TABLE 9

HEAT RESISTANCE OF VULCOLLAN *

Property	20° C	70° C
Tensile strength (kg. per sq. cm.)	311	191
Extensibility (percentage)	765	765
Stress at 300% elongation (kg. per sq. cm.)	78	49
Hardness (Shore)	69	64
Rebound resilience (percentage)	64	58
Structural strength (kg. per sq. cm.)	175	125

* This particular Vulcollan was the product of ethyleneglycol-adipic acid polyester and naphthylene-1,5-diisocyanate.

However, when heated above 200° C, Vulcollan is profoundly altered, probably because of the relative instability of the isocyanate bonds[29].

Turning once more to the mechanical properties of Vulcollan, its resistance to abrasion is excellent; *e.g.*, it is better than that of the best types of Buna, in fact better than natural rubber itself. Accordingly Vulcollan may ultimately prove to be an outstanding material for products which are subject to severe wear, *e.g.*, the heels of shoes. Another important property of Vulcollan is the low permeability of its films to gases, which is only $\frac{1}{10}$ to $\frac{1}{20}$ that of a comparable film of natural rubber. Vulcollan tubing has been made successfully, where advantage may be taken of these favorable characteristics. Of importance also is the very small damping effect shown by Vulcollan, *i.e.*, less energy is converted into heat than with either Buna or natural rubber.

One disadvantage of Vulcollan is that its properties can be modified less by the addition of compounding ingredients than can those of butadiene polymers. The specific gravity is 1.2, and is therefore higher than the specific gravities of conventional rubbers. When stretched, Vulcollan, shows like natural rubber a well defined x-ray diagram not shown by any of the Buna types, except cold polymers. A stiffening effect which appears under certain conditions is also evident by roentgenographic analysis.

It is obvious that Vulcollan has its merits and its shortcomings, and in general the requirements of manufacture, which have been merely touched upon in this paper, will be the deciding factor. To a certain extent methods wholly new to the rubber industry must be adopted, and these will doubtless tend at first to make the extensive use of Vulcollan slower. Obviously, however, the new technical results which can be obtained would seem to justify a change to new methods of operation, which in some cases may be simpler than before. Finally the price of Vulcollan is an important factor in its large-scale use. At a time when natural rubber is available at a low price, and with the pressing

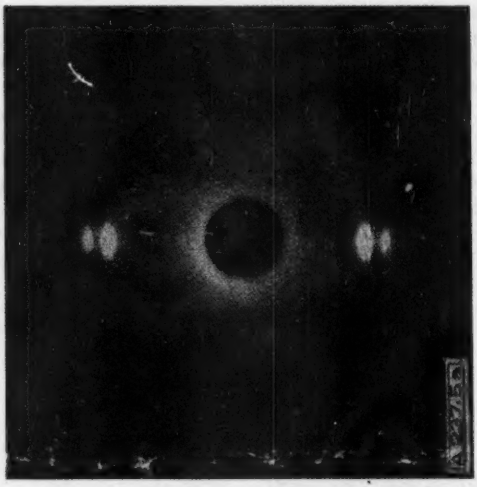


FIG. 5a.—Vulcollan from ethyleneglycol-adipic acid polyester, stretched 1:5. Well defined fiber diagram highly crystalline.

FIG. 5b.—Vulcollan from propyleneglycol-adipic acid polyester, stretched 1:5. Parallel alignment of chains, but essentially amorphous.

decisions which the industry is being called upon to make, the economic problem cannot be definitely answered.[34]

ELASTOMERS OF THE POLYESTER SERIES OF A DIFFERENT STRUCTURE

Investigations have been going on in different countries since 1938 on rubber-like materials derived from polyesters, and two types must now be distinguished.

One line of investigation has been concerned with polyesters having network structures, which are prepared without the addition of isocyanates; in the other line of investigation, polyesters, likewise with network structures, have been used in conjunction with diisocyanates[35].

With reference to the types of polyester elastomers prepared without isocyanates, the work of Karl Wolf should be mentioned first. In 1938–40, Wolf was occupied with a detailed investigation of polyesters from dicarboxylic acids on the one hand, and of tervalent alcohols on the other, and he found that polyesters having network structures form, with adipic acid, glycol, and glycerol, products having rubberlike elasticity. Although these products have found technical application in the manufacture of linoleum, they have little strength and tear resistance.

In a comprehensive confidential report of the Scientific Commission on Rubber of the former I.G.-Farbenindustrie, dated July 22, 1943, Wolf has dealt thoroughly with the theoretical principles involved in the phenomenon. Based on his conclusions, it should be possible to improve the mechanical properties of these elastomers, provided it is possible to increase considerably the chain length of the polyesters and, consequently, to increase the distance apart of the points of network structure. These predictions of Wolf have been thoroughly confirmed by the investigations of the present authors on Vulcollan.

Investigations have also been carried out in the laboratories of the Bell Telephone Company on polyesters containing small proportions of unsaturated components. For example, an ethyleneglycol-sebacic acid polyester condensed with up to 3 per cent of maleic acid has been synthesized[36]. This product can be converted into a product having a network structure and the elastic properties of rubber by heating with benzoyl peroxide. In this case C—C bonds are apparently united between the individual linear polyester chains[37]. The resulting product has been placed on the market under the name of Paracone. By loading with calcium carbonate or iron oxide, the mediocre mechanical properties are improved, and tear resistance values up to 130 kg. per sq. cm. have been obtained. However, these products have apparently not attained any real technical importance.

More important are the polyesters which are modified by diisocyanates. In addition to the German products, isocyanate rubbers, and Vulcollan which have been described, elastomers have been developed on the same principles in America and in England. E. I. du Pont de Nemours & Co. has a patent[38] for the transformation of polyesters and polyester amides by an excess of diiso-(thio)cyanates into what are said to be cross-bonded polymers. The part played by water in the network reaction as described in the present work was evidently not recognized, because the claim is that the reaction is preferably to be carried out with exclusion of oxygen and moisture. Apparently work elsewhere than in Germany has been carried on with polyester amides. For example, polyester amides from adipic acid, ethyleneglycol, and monoethanolamine have been used by E. I. du Pont de Nemours & Co., and by Imperial Chemical Industries, Ltd. The ester, previously condensed to a molecular weight of 5000, is extended with the theoretical proportion of a diisocyanate, and the product, which still has a linear form, is transformed in a final separate step into a product having a network structure. In this final reaction, formaldehyde of an agent generating formaldehyde, a dichromate, or even a polyisocyanate is used. Formaldehyde attacks the amido residues of the amide ester. The final product, which has no structural strength worthy of note, bears the

name of Vulcaprene, and it has been used for the impregnation of fabrics and in lacquers[39].

Recently other rubberlike products prepared from polyesters of dimerized or polymerized soybean oil which have been further transformed by diisocyanates have been described[40].

The mechanical properties of Vulcollan have not even been approached by the American products[41].

Later, in due course of time, further progress and developments in this field will be reported, and the theoretical principles established by the authors, together with technical applications of the products, will be discussed.

SUMMARY

It is shown that new types of highly elastic products with remarkable properties can be obtained by a process of diisocyanate poly-addition, which involves the transformation of linear polyesters of glycols and dicarboxylic acids with an excess of certain special "expansive" diisocyanates in the presence of a very small proportion of water. The terminally bifunctional polyesters react first with the diisocyanate, with resultant lengthening of the chains. A network is subsequently developed from urea groups, which are formed from isocyanate groups and water, and which then react with the diisocyanate.

The chemical mechanism of this process is discussed in detail. In addition, the processing and possible applications of this new class of elastomers is reviewed.

REFERENCES

[1] Bayer, Rinke, Siefken, Orthner, and Schild, German patent 728,981 (Nov. 11, 1937).

[2] For polyfunctional esters as raw materials for lacquers, see Bunge, Bayer, Petersen, and Spielberger, German patent 756,058 (Mar. 1940). For polyfunctional esters as molding materials, see Höchtlen, Petersen, Bunge, and Bayer, German patent application I-66,946 (May 1940); French patent 873,780. For a complete description, see *Angewandte Chemie* **59**, 257 (1947).

[3] Hofman, German patent 318,222.

[4] Carothers, Collected Papers, edited by Mark and Whitby, Interscience Publishers, Inc., New York, **1940**.

[5] Fuller and collaborators, *J. Am. Chem. Soc.* **59**, 344 (1937); **61**, 2575 (1939); **70**, 421 (1948); *Ind. Eng. Chem.* **30**, 472 (1940); *Chem. Revs.* **26**, 143 (1940); *J. Chem. Education* **20**, 3 (1943).

[6] Terylene (Imperial Chemical Industries, Inc.) is the trade name for the high melting and stringy polyester of ethyleneglycol and terephthalic acid (see British patents 578,079 and 579,462); see also Whinfield and Dickson, *Nature* **158**, 871, 930 (1946); Hardy, *J. Soc. Chem. Ind.* **67**, 426 (1948); *Silk and Rayon* **1946**, p. 1386; **1947**, p. 1396.

[7] Staudinger and Berndt also have studied the structure of linear polyesters (see *J. Makromol. Chem.* **1**, 22 36 (1947)) and have come to the conclusion that strictly linear polyesters also are apparently branched. The present authors cannot agree with this view, for, according to our opinion, such polyesters formed from purely bifunctional components are always linear. The diisocyanate reaction may represent the most sensitive reagent to detect even slight degrees of network formation.

[8] Schlack, German patent application J-66,330 (Jan. 17, 1940); French patent 859,243.

[9] Schlack, German patent application J-66,330 (Jan. 17, 1940); French patent 869,243; Christ and Hanford, U. S. patent 2,333,639 (June 6, 1940).

[10] Pinten (Dynamit Nobel A.-G.), German patent application D-90,260 (Mar. 13, 1943).

[11] Reiss, *Physik. Blätter* **3**, 220 (1947).

[12] This phenomenon, which has been familiar to the present authors for a long time, has recently been termed high molecular thixotropy by Müller (*Kolloid-Z.* **112**, 1 (1949). A new method for measuring the hardening effect (stiffening and crystallization) of these ester rubbers has been developed by W. Brenschede in the laboratory of the present authors. In this method the elasticity and hardness of the test-specimens are measured while the specimens are stretched. When elongated, the specimens show a considerably greater tendency to crystallize. This rapid method was found to be highly important in carrying out the synthetic work.

[13] Müller, Petersen, and Bayer, German patent application J-76,584 (Jan. 17, 1944). The claims include a process for the preparation of high-molecular synthetic products having the characteristics of vulcanized rubber or having leatherlike properties, and formed in principle by the reaction of linear macro compounds having molecular weights of at least 1000, and terminal hydrogen atoms which are reactive with diisocyanates which have at least one nitro group in the molecule.

[14] The trade name of this compound is Desmodur-15.

[15] Petersen, Müller, and Bayer, German patent application J-77,229 (April 12, 1944). The claim is a process for the preparation of rubberlike materials formed by the reaction of preponderantly linear polyesters (from glycols and aliphatic dicarboxylic acids, neither of which component contains more than seven carbon members), with diisocyanates or compounds of the carboxycyclic or heterocyclic series which contain at least two condensed rings. For the preparation and the constants of the diisocyanates, see Siefken (*Ann.* **562**, 75 (1949)). Naphthalene-1,5-diisocyanate (melting point 132°) is preferable to aliphatic diisocyanates and diisocyanates of the benzene series because its low vapor pressure makes it less toxic. It is also one of the most reactive of the isocyanates.

[18] See, for example, Mark, *Am. Dyestuff Reporter* **36**, 323, 326 (1947).

[17] These views are supported by work on a polyester amide prepared from adipic acid and a mixture of glycol and piperazine which is described later, whereby, with hexamethylene diisocyanate, highly elastic masses with good tensile properties are obtained. In this case, therefore, the structurally expansive piperazine would be the separating agent.

[18] See also Bayer and Bunge, German patent application J-76,587 (Jan. 4, 1944).

[19] Bayer, Müller, Piepenbrink, Windemuth, Bunge, and Petersen, German patent application J-77,781 (July 10, 1944). The patent claims a process for the preparation of high-molecular elastic materials, involving the reaction of a linear polyester composed of predominantly aliphatic constituents, which may, in addition, contain in the polyester chain hetero-atoms, aromatic, hydroaromatic, and heterocyclic ring systems, with a larger quantity of a diisocyanate than the quantity necessary for merely increasing the chain length, care being taken that at the beginning, or at an intermediate stage of the reaction with the diisocyanate, urea groups are formed and incorporated in the molecule.

[20] Kühn, *Ber.* 17, 2881 (1884); Petersen, *Ann.* **562**, 214 (1949); Bayer, *Angew. Chem.* **59**, 263 (Footnotes 19–21) (1947); Kühn and Henschel, *Ber.* **21**, 504 (1888).

[21] Windemuth, German patent application J-75,922 (Sept. 22, 1943).

[22] The possibility of using either pure or mixed esters was investigated by H. Havekoss and F. Schmidt in addition to the work by the present authors.

[23] This applies also to the Troisdorfer isocyanate elastomer. See Müller and Traube, German patent application J-77,127 (Apr. 3, 1944). This patent claims a process for the preparation of products ranging from rubberlike to leatherlike in character by the reaction of diisocyanates with polyesters which have been formed essentially from bifunctional components by condensation with a small proportion of a multiple functional component; the esters used have molecular weights of at least 1000, and are liquid at room temperature.

[24] In a patent of Müller, Bayer, and Piepenbrink (German patent application J-76,823, Feb. 14, 1949) experiments on the vulcanization of ester elastomers containing unsaturated constituents by the addition of sulfur are described.

[25] Fuller, *Ind. Eng. Chem.* **30**, 472 (1938).

[26] Windemuth, Bayer, and Bunge, German patent application J-75,952 (Oct. 4, 1943). The patent claims a process for the preparation of molded masses, including lacquers, coatings, and similar products, formed from polyesters of essentially linear structure and which contain reactive hydrogen united to the nitrogen atoms by reaction with polyfunctional isocyanates under conditions whereby the masses are simultaneously or previously molded into shape, and whereby the numbers of reactive hydrogen atoms and of isocyanate groups are so formulated that fusible reaction products are no longer formed.

[27] Carothers, U. S. patent 2,130,948 (1938); Lieser, Gehlen, and Gehlen-Keller, *Ann.* **556**, 114 (1944).

[28] According to measurements by H. Rinke, the urethan hydrogen atom in simple model experiments reacted about 80–100 times more slowly than did a hydrogen atom of the urea bridge.

[29] Petersen, *Ann.* **562**, 209 (1949).

[30] Bayer, Havekoss, Piepenbrink, Windemuth, Petersen, and Bunge, German patent application (Jan. 16, 1945; no number assigned). The patent claims a process of adhesion which involves coating the materials to be adhered with solutions of condensation products, prepared in the absence of water, from linear polyesters and diisocyanates, and then allowing these condensation products to harden, under the influence of moisture or of diamines and in addition, if necessary, of heat and pressure, in contact with the materials to be adhered.

[31] For the literature, see *Angew. Chem.* **59**, 267 (1947); footnotes 47–49 and 70.

[32] Bayer, German patent application J-77,394 (May 15, 1944). This patent claims a process for the preparation of high-molecular compounds by the reaction of bis- and polyfunctional isocyanates with compounds which contain two or more hydrogen atoms, reactive with isocyanates, and featured by the fact that the condensation and shaping of the final article are brought about wholly or in part by the action of centrifugal forces.

[33] Wildschut, "Technological and Physical Investigation of Natural and Synthetic Rubber", Elsevier Publishers, New York, **1946**.

[34] The work on the technical applications of Vulcollan during its development was carried out under the supervision of E. Konrad on an extensive scale in the lacquer and synthetic materials testing department and in the central rubber laboratory at Leverkusen. A. Höchtlen and H. Pfeffer took a particularly active part in this work, as did E. Weinbrenner and C. Mühlhausen subsequently.

[35] See also *Angew. Chem.* **59**, 269 (1947); literature references 75–80.

[36] Biggs, Erickson, and Fuller, *Ind. Eng. Chem.* **39**, 1090 (1947).

[37] Baker, *J. Am. Chem. Soc.* **69**, 1125 (1947).

[38] Christ and Hanford, U. S. patent 2,333,639 (June 2, 1940); Windemuth, Bayer, and Bunge, German patent application J-75,952 (Oct. 4, 1943). For the claims of this latter, see Reference no. 26 in the present paper.

[39] The Imperial Chemical Industries patents include: Coffey, Cook, and Lake, British patent 574,134 (Oct. 26, 1942); Smith, Buist, Harper, and Welding, British patent 581,143 (Dec. 21, 1942); Furness and Perrins, British patent 581,144 (Feb. 10, 1943); Coffey and White, British patent 581,146 (June 25, 1943); Smith, White, and Harper, British patent 585,083 (Feb. 28, 1945). See also Harper, Smith, and White, *Proc. Second Rubber Technol. Conf.* (London), **1948**, p. 61; British patent 585,205. The E. I. du Pont de Nemours & Co. patent is that of Vaala and Frank, U. S. patent 2,422,271 (1943).

[40] Cowan, Wheeler, Teeter, Paschke, Scholfield, Schwab, Jackson, Bull, Earle, Foster, Bond, Beal, Skell, Wolff, and Mehltretter, *Ind. Eng. Chem.* **41**, 1647 (1949).

[41] The results obtained in the work of the present authors has in part been made known outside of Germany by reports of the FIAT. See "The Rubber Industry in Germany", British Intelligence Objectives Overall Report No. 7; BIOS Final Report No. 1166 (Interrogation of August 1946; CIOS File XXV-34). See also *Modern Plastics*, **1945**, p. 152.

OXIDATION OF COMPOUNDS STRUCTURALLY RELATED TO GR-S *

J. W. LAWRENCE AND J. REID SHELTON

CASE INSTITUTE OF TECHNOLOGY, CLEVELAND, OHIO

The oxidation of GR-S type synthetic rubber has been studied extensively[1], but because of the complex nature of the material, it is difficult to interpret the results in terms of actual chemical reactions. The successful use of information obtained in the oxidation of pure organic compounds to help explain the behavior of more complex systems has been demonstrated by previous workers[2], and has resulted in important contributions, particularly in the field of polyisoprene oxidation. The present investigation was undertaken in an effort to obtain more detailed knowledge of the probable reactions involved in the oxidation of GR-S by means of a study of the oxidation of compounds structurally similar to GR-S.

The structural relationship between the compounds studied and GR-S is shown in Figure 1. 1-Phenyl-4-hexene and 1-phenyl-3-pentene correspond to

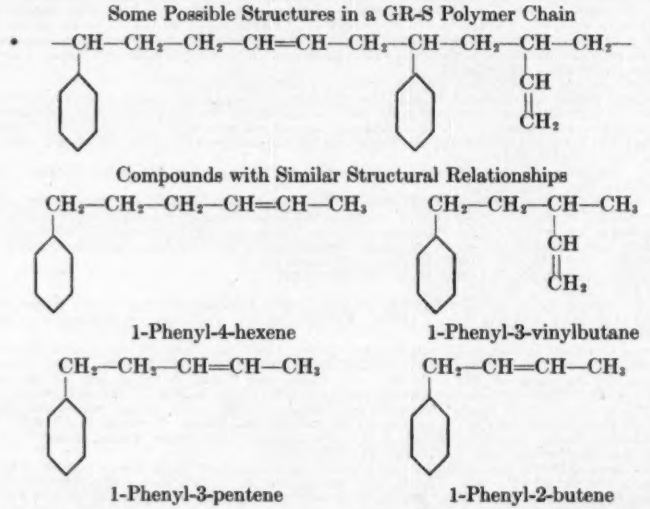


FIG. 1.—Comparison of a series of unsaturated compounds with some structural units in GR-S.

the structures formed in a 1,4-copolymerization of butadiene with styrene. 1-Phenyl-3-vinylbutane represents a possible structure resulting from 1,2-polymerization of the diene. 1-Phenyl-2-butene was included to complete the sequence 1–4, 1–3, and 1–2 with respect to the structural relationship between

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 42, No. 1, pages 136–140, January 1950.
The present address of J. W. Lawrence is the Atlas Powder Co., Tamaqua, Penna.

the phenyl radical and the point of unsaturation. The deviation from the preferred I.U.C. system of numbering in the above names is intended to emphasize these structural relationships.

The volumetric method of oxygen absorption employed in this investigation involves measurement of the change in volume at constant temperature and pressure. The method has been employed by previous workers; however, the present study differs from reported research in two respects—namely, the size of the sample and the method of stirring. Bolland and Gee[3] made oxidation-rate observations on 0.2-gram samples of hydrocarbon; George and Robertson[4] used 1-gram samples. The hydrocarbon sample used in this research was 10 to 20 grams. Farmer[5] and the above-mentioned investigators employed a system in which the hydrocarbon was agitated in an oxygen atmosphere so that diffusion was not a factor. In this research a large excess of oxygen was circulated through the hydrocarbon with provision for the recirculation of the unreacted oxygen.

OXYGEN-ABSORPTION MEASUREMENTS

The apparatus used for the oxygen-absorption determinations is shown in Figure 2. This equipment is essentially the same as that described by Dornte[6] for the oxidation of lubricating oils.

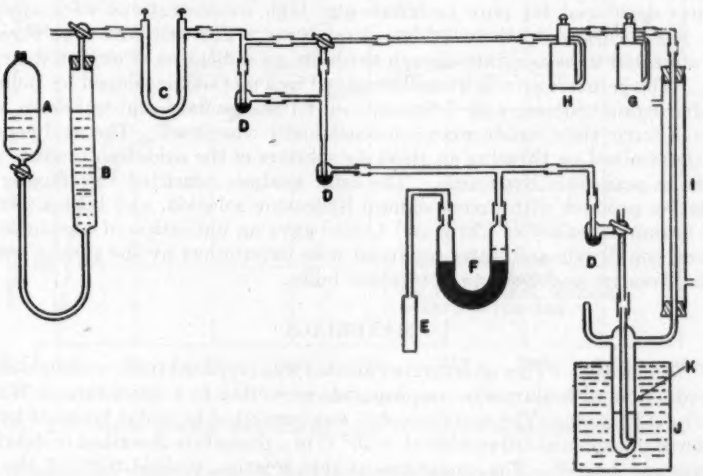


FIG. 2.—Oxygen-absorption apparatus.

The oxygen circulation was accomplished by a bellows pump, *E*, directly connected to a geared motor (Merkle-Korff Gear Company, Chicago, Ill., 110-volt, alternating current, 50 r.p.m.). Three mercury valves, *D*, controlled the unidirectional flow of the oxygen as the alternate compression and expansion of the bellows was transmitted through *F* to the system, thus permitting recirculation of the unreacted oxygen.

The oxygen was circulated at the rate of 50 cc. per minute. The absorption tube, *K*, containing 10 to 20 grams of hydrocarbon, was maintained at 100° ± 0.1° C in a constant-temperature bath, *J*. Intimate contact between the gas stream and the hydrocarbon was assured by introducing the oxygen through a

fritted-glass filter at the bottom of the absorption tube. A condenser, *I*, above the absorber returned refluxing hydrocarbon. Water and carbon dioxide formed during the oxidation were removed from the gas stream by Drierite, *G*, and Ascarite, *H*. The oxygen absorbed was measured in a gas buret, *B*, with a saturated aqueous solution of sodium acetate as the confining liquid. Oxygen from the buret entered the system through a Drierite tube, *C*, to replace oxygen absorbed by the sample. The measurement was made by stopping the pump, equalizing the pressure in the system, and bringing the pressure of the system to 76 cm. of mercury with the sodium acetate solution leveling bulb, *A*. The operation of the system was suspended for about a minute to take the reading.

The procedure for beginning a run consisted of weighing the hydrocarbon into the absorption tube, displacing the air in the tube with nitrogen, and connecting the absorber into the system with Tygon plastic tubing. When the absorber contents reached the bath temperature the nitrogen was displaced with oxygen, the necessary valve adjustments were made, and the pump was started.

ANALYSIS OF OXIDATION PRODUCTS

The viscous, dark oxidation product was analyzed for groups containing oxygen. From the analyses an oxygen balance was made. Analytical procedures developed for pure materials and high concentrations were applied, with less accuracy, to these oxidation mixtures. The analyses were checked and appeared to be accurate enough to obtain an indication of oxygen distribution. The peroxide groups were determined by a method developed by Bolland, Sundralingam, Sutton, and Tristram[7], in which standard and unknown solutions of ferric thiocyanate were colorimetrically compared. The acid content was determined by titrating an alcoholic solution of the oxidation product with alcoholic potassium hydroxide. The ester analysis consisted in refluxing the oxidation product with excess sodium hydroxide solution, and back-titrating. The bromine method of Uhrig and Levin[8] gave an indication of unsaturation. The carbon dixode and water produced were determined by the gain in weight of the Ascarite and Drierite absorption bulbs.

MATERIALS

Crotyl alcohol.—This unsaturated alcohol was prepared from crotonaldehyde by reduction with aluminum isopropoxide according to a procedure of Wilds[9].

Crotyl bromide.—The crotyl alcohol was converted to crotyl bromide by the action of phosphorus tribromide at −20° C in a procedure described in detail by Young and Lane[10]. The conditions of this reaction yielded 95% of the unsaturated halide in the form of the crotyl bromide rather than its isomer, 3-bromo-1-butene.

3-Bromo-1-butene.—This isomer of crotyl bromide was produced by the slow fractionation of crotyl bromide as described by Young and Lane[10].

1-Phenyl-2-butene.—Phenyl magnesium bromide was prepared from 13 grams of magnesium and 79 grams of bromobenzene in 400 cc. of ether in a round-bottomed 3-necked flask with stirring. Sixty grams of crotyl bromide, preserved at 0° C, was added, and the mixture was finally hydrolyzed with 10% hydrochloric acid. The unsaturate was extracted with ether, the ether evaporated, and the product distilled in a glass helix-packed 18-inch column. A 34% yield of 1-phenyl-2-butene, boiling at 69–70° C at 12 mm., was obtained.

1-Phenyl-3-vinylbutane.—The conditions of the Grignard reaction were essentially as described above, except that β-phenyl ethyl magnesium bromide was produced. This Grignard reagent reacted with crotyl bromide to produce a material boiling at 90–92° C at 13 mm. The product from the oxidation of the ozonized unsaturate was a noncrystallizing oil. However, the amide of the oil melted sharply at 118° C, which compares with 118° C given in Beilstein as the melting point of γ-phenyl-α-methyl butyric acid amide.

1-Phenyl-4-hexene.—The Grignard reagent of β-phenyl ethyl bromide reacted with 3-bromo-1-butene to produce an unsaturate boiling at 93–95° C at 12 mm. The acid from the oxidized oxonized unsaturate melted at 50° C, and showed no depression in melting point when mixed with α-phenyl butyric acid.

1-Phenyl-4-pentanol.—γ-Phenyl propyl magnesium bromide reacted with an excess of acetaldehyde in a round-bottomed 3-necked flask with stirring. After hydrolysis, the secondary alcohol was extracted with ether and distilled once in a Vigreux column. A 75% yield of 1-phenyl-4-pentanol, boiling at 127–128° C at 6 mm., was isolated.

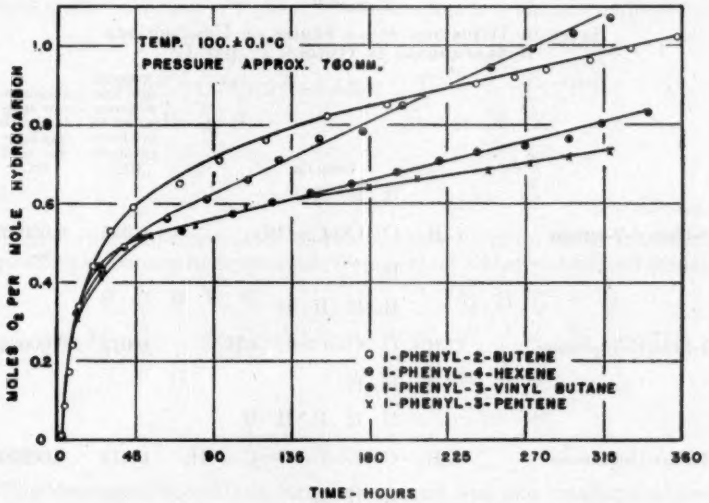


FIG. 3.—Variation of oxygen absorption with time for a series of unsaturated hydrocarbons.

1-Phenyl-4-bromopentane.—The 1-phenyl-4-pentanol was treated with phosphorus tribromide, 1 mole of alcohol to ⅓ mole of phosphorus bromide. Water was added after completion of the reaction, and the bromide was separated, dried, and distilled. A 62% yield of material, boiling at 110–112° C at 2 mm., was secured.

1-Phenyl-3-pentene.—The 1-phenyl-4-bromopentane was refluxed for 3 hours with an alcoholic potassium hydroxide solution. The caustic was used in the ratio of 2.5 to 1 mole of halide, and 6 moles of anhydrous ethyl alcohol to 1 mole of halide. The alcohol was removed by warming under vacuum, and water was added to dissolve salt and caustic. The unsaturate was extracted with ether and distilled in a small glass helix-packed column. A 35% yield of unsaturate, boiling at 87–89° C at 13 mm., was obtained.

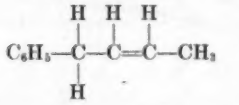
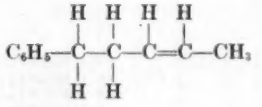
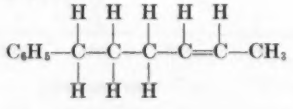
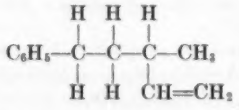
The oxidized ozonized product from the unsaturate was an oil which crystallized slowly on standing. The product, recrystallized from petroleum ether, melted at 47° C. The mixed melting point with γ-phenyl butyric acid showed a large depression, so the identity of the compound as β-phenyl propionic acid was indicated.

COMPARISON OF OXIDATION RATES

The variation of oxygen absorption with time for the four unsaturated hydrocarbons is shown in Figure 3. The plots of oxygen absorption with time show two distinct stages apart from the very short induction period: the autocatalytic stage in which peroxides are formed in quantity and in which the oxidation rate is increasing, and a stage in which the oxidation rate is approximately constant and the principal reactions are the formation of secondary products. The induction period, which precedes the autocatalytic stage, involves such a small amount of time and oxygen in the case of these pure compounds that no conclusions can be drawn concerning it.

TABLE I

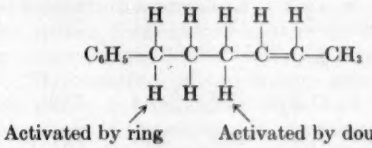
RATES OF OXIDATION FOR A SERIES OF UNSATURATED HYDROCARBONS IN OXYGEN AT 100° C

	Formula	Average rate first 40 hours (moles O_2 per hour per mole HC)	Constant-rate stage (moles O_2 per hour per mole HC)
1-Phenyl-2-butene		0.015	0.00097
1-Phenyl-3-pentene		0.012	0.00064
1-Phenyl-4-hexene		0.013	0.00200
1-Phenyl-3-vinylbutane		0.013	0.00100

The transition from the autocatalytic stage to the lower constant-rate stage occurs after approximately 40 hours at 100° C in each case; consequently, the amount of oxygen absorbed at this point was taken as an arbitrary basis for comparison of the relative oxidizability of the compounds in the autocatalytic period. In the constant-rate stage the slope of the linear portion of the curve is a direct measure of the relative oxidizability in that stage. These data are summarized in Table I.

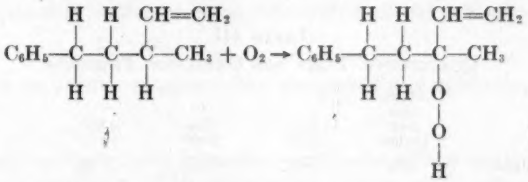
The more extensive oxidation of 1-phenyl-2-butene in the autocatalytic stage is probably due to the presence of an α-methylene group activated by

both the double bond and the aromatic nucleus. The oxidizability of the other compounds is determined by two α-methylene groups per molecule. One group is activated by the ring, while the other is acted upon by the double bond as indicated below for 1-phenyl-4-hexene:

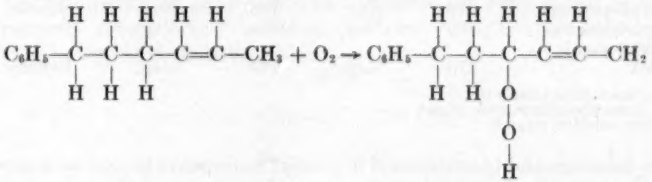


The cumulative effect of these two separate centers of activation upon two carbon atoms evidently is not so great as the influence of both centers on the same carbon as in the oxidation of 1-phenyl-2-butene.

In the constant-rate portion of the oxidation curve, the phenyl-hexene isomers showed widely different rates. The straight-chain isomer oxidized twice as fast as the branched-chain isomer. One of the probable products formed in the oxidation of 1-phenyl-3-vinylbutane is a tertiary hydroperoxide:



This tertiary hydroperoxide would probably be more stable than the corresponding secondary hydroperoxide formed from 1-phenyl-4-hexene oxidation:



The decomposition of the latter compound and the resultant secondary oxidation reactions may account for this observed behavior.

SEQUENCE OF OXIDATION PRODUCTS

This discussion is primarily concerned with the reactions of 1-phenyl-2-butene, although the general reaction pattern can probably be applied to the other compounds of the series. Intermediate oxidation products of 1-phenyl-2-butene proved to be easier to isolate than the products of the oxidation of the other compounds of the series; consequently, this compound was studied in greater detail than the others.

Primary oxidation products.—Table II, summarizing the oxygen distribution in the separate runs, indicates that 65 per cent of the oxygen absorbed by the unsaturate 1-phenyl-2-butene was in the form of peroxides when the reaction time was 6 hours. The nonperoxidic oxygen was in the form of acids, ketones, and aldehydes as revealed by qualitative tests, whose results are shown in Table III. Thus, peroxides appear to be the primary products, and other com-

TABLE II

DISTRIBUTION OF OXYGEN AMONG OXIDATION PRODUCTS

	Oxidation time (hours)	Acid (%)	Ester (%)	CO_2 (%)	H_2O (%)	Peroxide (%)	total oxygen[a] accounted for (%)
1-Phenyl-2-butene	6	20.2	..	..	..	65	85.2
1-Phenyl-2-butene	359	11.3	42.6	9.4	19.6	4.2	87.1
1-Phenyl-3-pentene	316	7.37	28.2	35.7	14.1	6.7	92.0
1-Phenyl-4-hexene	369	9.1	34.2	18.6	34.1	4.0	100.0
1-Phenyl-3-vinylbutane	370	10.7	37.5	16.3	28.7	4.3	97.5

[a] Percentages represent fractions of total oxygen found in various products. Total oxygen was determined by absorption, not analysis.

pounds such as acids, esters, ketones, aldehydes, carbon dioxide, and water appear to result from secondary reactions in the attack of unsaturates by molecular oxygen.

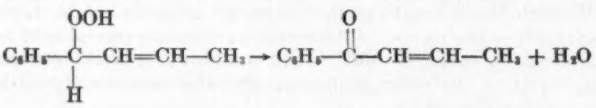
TABLE III

QUALITATIVE TESTS FOR OXIDATION PRODUCTS

	Oxidation time (hours)	Alcohol[a]	Ketone[b]	Aldehyde[c]	Compounds isolated
1-Phenyl-2-butene	359	Neg.	Pos.	Neg.	Benzoic acid, phenyl 1-propenyl ketone
1-Phenyl-2-butene	6	Neg.	Pos.	Pos.	Phenyl 1-propenyl ketone
1-Phenyl-3-pentene	316	Neg.	Pos.	Neg.	Benzoic acid
1-Phenyl-4-hexene	369	Neg.	Pos.	Neg.	Benozic acid
1-Phenyl-3-vinylbutane	370	Neg.	Pos.	Neg.	Benzoic acid

[a] Ceric ammonium nitrate test.
[b] 2,4-Dinitrophenylhydrazine reagent.
[c] Fuchsin aldehyde reagent.

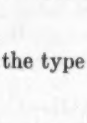
The isolation and identification of phenyl 1-propenyl ketone as a product of the oxidation of 1-phenyl-2-butene are good evidence of the formation of an α-methylene hydroperoxide. Quantitative data on the yield of ketone were not obtained, and this accounts at least in part for the smaller percentage of oxygen accounted for in Table II in the case of 1-phenyl-2-butene. The formation of ketones from peroxides under the proper conditions of temperature has been reported by others[11]. The reaction may be represented as follows:

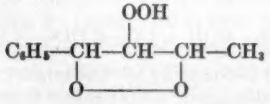


The 6-hour run with 1-phenyl-2-butene has not been included in Figure 3, which relates time and oxygen absorption for the longer runs, because the plot for this run did not correspond with the plot for the longer run. The sample of 1-phenyl-2-butene employed for the shorter run was subjected to more exhaustive purification by fractional distillation than were the samples represented in Figure 3. To secure exact reproducibility in the initial stage, a method of

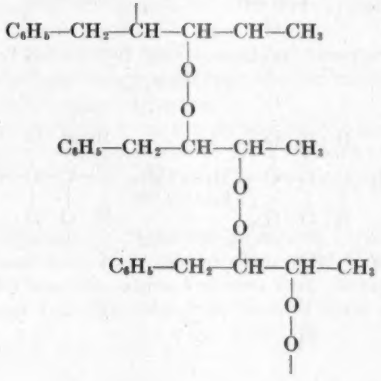
purification such as chromatographic absorption would probably have to be employed.

The 6-hour run gave a total absorption of 0.5 mole of oxygen per mole of 1-phenyl-2-butene. Titrations with bromine indicated that only about 57 per cent of the initial unsaturation remained at the end of this short run. Reactions which might reduce unsaturation include polymerization of the hydrocarbon, oxidative scission at the double bond, and peroxide formation involving the double bond. Hydrocarbon polymerization seemed unlikely, however, in the case of a fairly stable, nonconjugated olefin such as 1-phenyl-2-butene, although it may take place to some extent in the presence of peroxides. Under the conditions of this experiment with an excess of oxygen present, the reaction of free radicals with oxygen would probably take place more readily than the reaction of free radicals with the olefin. Chain scission with the formation of acids would require 4 atoms of oxygen per double bond and only about 0.5 per cent of the hydrocarbon would be required to account for the 20 per cent oxygen found in acids in the 6-hour run. Thus neither of the first two postulated reactions is likely to be the major factor in this initial reduction in unsaturation.

The observed reduction in unsaturation simultaneous with the production of peroxides apparently indicates some interaction of oxygen with the double bond. Direct saturation to give a four membered ring of the type  is possible. Polymeric or cyclic peroxides would also reduce unsaturation while giving peroxide reactions. The only intramolecular cyclic peroxides possible from 1-phenyl-2-butene would have either four or five atoms in the ring, whereas the cyclic peroxides described in the literature usually involve a six-membered ring. Cyclic diperoxides have also been suggested by Farmer and co-workers according to a recent review[12], and in the case of 1-phenyl-2-butene might possess the following structure:

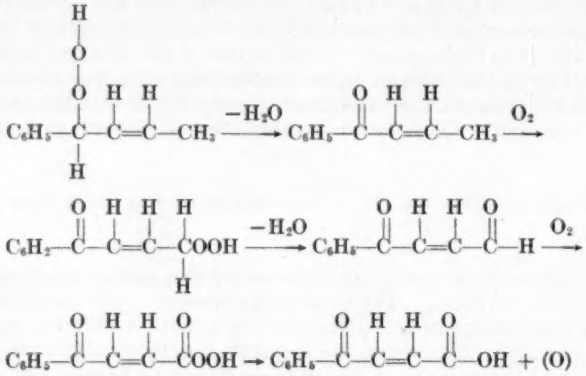


There is good evidence of the existence of polymeric peroxides[13], and thus it is probable that some of the peroxide was of this type. A possible structure would be:

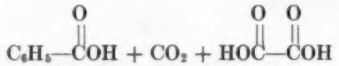


The primary reactions thus appear to involve the formation of peroxides. However, the evidence indicates that either cyclic or polymeric peroxides or both are formed as well as the α-methylene hydroperoxide.

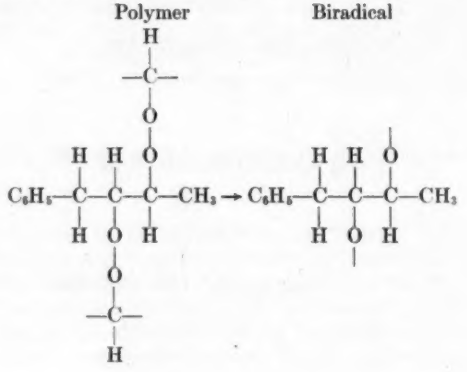
Secondary oxidation products.—Secondary products found in the oxidation of 1-phenyl-2-butene were phenyl 1-propenyl ketone, ester, benzoic acid, carbon dioxide, and water, as shown in Tables II and III. The ketone, as previously indicated, is probably one of the first decomposition products of α-methylene hydroperoxide of 1-phenyl-2-butene. Phenyl 1-propenyl ketone, which was synthesized independently, was oxidized at 100° C until one atom of oxygen per mole of ketone had been absorbed. The identified products from this oxidation were benzoic acid, carbon dioxide, and water. No test for ester was secured from this oxidation mixture. A sequence of compounds which would be chemically reasonable and which would include the indicated products is:



Oxidation scission might then yield

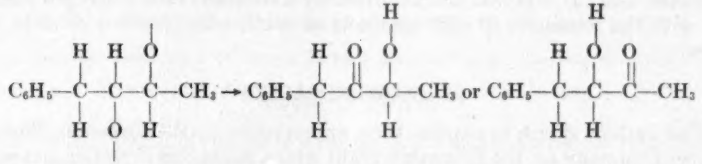


The secondary product accounting for the largest portion of the oxygen was the ester. This class of compounds might result from the decomposition of the peroxide polymer. Peroxide polymer decomposition would yield molecular fragments, such as the following biradical:



When the peroxide linkage has split as indicated above, two possibilities for further change are apparent: isomerization to a ketol as described by Morell and coworkers[14], and removal of hydrogen atoms from the surroundings to give a dialcohol.

The reaction for ketol formation is:



The absence of alcohol as noted in Table III may result from conversion to ester in the presence of excess acid resulting from oxidation of ketone, ketol, or other intermediates. The formation of large amounts of ester without increase in acid concentration suggests that the decomposition of the polymeric peroxide results in the formation of ester, carbon dioxide, and water as the utlimate products.

Further work is in progress on the oxidation of certain of these compounds. It is hoped to obtain more complete analytical data at various stages of oxidation and thus establish more precisely the sequence of reactions involved.

SUMMARY AND CONCLUSIONS

1-Phenyl-2-butene oxidized more extensively in the autocatalytic stage at 100° C than did 1-phenyl-3-pentene, 1-phenyl-4-hexene, and 1-phenyl-3-vinylbutane. Thus it appears that the double activation of a single methylene group by both the phenyl group and the olefin group produces peroxide more readily than does the simultaneous activation of separate methylene groups by these same structures.

The relative order of oxidizability in the subsequent period of slower constant-rate oxygen absorption is: 1-phenyl-4-hexene highest; 1-phenyl-2-butene and 1-phenyl-3-vinylbutane about equal; and 1-phenyl-3-pentene slowest. The high rate for the 1-phenyl-4-hexene in this stage may be due to the presence of an additional methylene group available for further oxidation initiated by the decay of the peroxides initially formed.

The primary oxidation products of 1-phenyl-2-butene appear to be peroxides. In addition to the formation of α-methylene hydroperoxide, there appears to be some attack at the double bond to form either polymeric or cyclic peroxides, or both.

Phenyl 1-propenyl ketone and benzoic acid have been isolated as secondary oxidation products which probably result from the decomposition of the α-methylene hydroperoxide of 1-phenyl-2-butene.

Ester formation may result from the decomposition and concurrent oxidation of the polymeric or cyclic peroxides to yield alcohols and acids.

SUMMARY

The rates of oxidation of 1-phenyl-3-pentene, 1-phenyl-4-hexene, and 1-phenyl-3-vinylbutane have been measured at 100° C and 1 atmosphere of oxygen pressure. 1-Phenyl-2-butene has also been included to complete the sequence 1–4, 1–3, and 1–2 with respect to the structural relationship between

the phenyl radical and the point of unsaturation. Information concerning the course of the reaction was obtained both from the rate data and from chemical analysis of the oxidized products. Three stages of oxidation were noted: (1) a very short induction period; (2) an autocatalytic stage which is characterized by a rapidly increasing rate and in which the primary products appear to be peroxides; and (3) a period characterized by a constant rate of oxygen absorption with the formation of such products as acids, esters, carbon dioxide, and water.

ACKNOWLEDGMENT

The authors desire to express their appreciation to the Firestone Tire and Rubber Company for the fellowship grant which made this investigation possible. They also wish to thank Hugh Winn, formerly of Case Institute of Technology and now with the Firestone Company, for the numerous helpful suggestions which he contributed in the course of this investigation.

REFERENCES

[1] Shelton and Winn, *Ind. Eng. Chem.* **36**, 728 (1944); **38**, 71, 1052 (1946); **40**, 2081 (1948).
[2] Farmer and Sutton, *J. Chem. Soc.* **1942**, p. 139.
[3] Bolland and Gee, *Trans. Faraday Soc.* **42**, 236 (1946); RUBBER CHEM. & TECHNOL. **20**, 611 (1947).
[4] George and Robertson, *Proc. Roy. Soc.* **A185**, 295 (1946).
[5] Farmer and Sundralingam, *J. Chem. Soc.* **1942**, p. 121.
[6] Dornte, *Ind. Eng. Chem.* **28**, 26 (1936).
[7] Bolland, Sundralingam, Sutton, and Tristram, *Trans. Inst. Rubber Ind.* **17**, 29 (1941); RUBBER CHEM. & TECHNOL. **15**, 72 (1942).
[8] Uhrig and Levin, *Ind. Eng. Chem. Anal. Ed.* **13**, 90 (1941).
[9] Wilds, "Organic Reactions," John Wiley & Sons, New York, **1944**, Vol. 2, p. 200.
[10] Young and Lane, *J. Am. Chem. Soc.* **59**, 2051 (1937).
[11] Cook, *J. Chem. Soc.* **1938**, p. 1778.
[12] Bolland and Hughes, *J. Chem. Soc.* **1949**, p. 492; Cole, J. O., paper presented the A.S.T.M. Symposium on Aging of Rubber, Chicago, Mar. 2, 1949; abstract in *Rubber Age* (N. Y.) **64**, 728 (1949); Am. Soc. Testing Materials, Special Tech. Publication, No. **89**.
[13] Farmer, *Trans. Inst. Rubber Ind.* **21**, 122 (1945); RUBBER CHEM. & TECHNOL. **19**, 268 (1946).
[14] Morell, *J. Soc. Chem. Ind.* **50**, 27T (1931).

STRUCTURE OF VULCANIZED LATEX *

N. C. H. HUMPHREYS AND W. C. WAKE

RESEARCH ASSOCIATION OF BRITISH RUBBER MANUFACTURERS, CROYDON, ENGLAND

INTRODUCTION

The vulcanization of rubber in latex form was first achieved by Schidrowitz[1] in 1921, and since then there has been considerable speculation on the structure of the continuous film formed by drying out the water. This film has, or has been claimed to have, most of the physical properties of vulcanized rubber prepared in the more usual way. Modern theories of rubberlike elasticity required a three-dimensional network of primary valency bonds, and it is difficult to see how this essential condition is fulfilled for dried-out vulcanized latex. Flint[2], in an excellent review of the vulcanized latex field, refers to Hauser's suggestion[3] that the adsorbed layer of protein and other nonrubber components remains coating the particles and, when the water is removed, acts as a cement holding the particles together. This view, as will be shown later, is improbable theoretically and is decisively disproved by the experimental work reported in this paper. Flint[2] records, however, that objections to this hypothesis were raised by von Weimarn[4] in 1928, though without experimental evidence, and van Dalfsen[5] states definitely that, in the case of vulcanized latex, "there is a discontinuous structure, consisting of latex particles which singly present a picture of normally vulcanized rubber held together, not by chemical bonds, but by van der Waal's forces".

As is well known, latex, like other emulsion systems, depends for its stability on the amphipathic nature of the material at the interface of the two phases. Let us consider the conditions for a substance to spread itself at an oil-water interface.

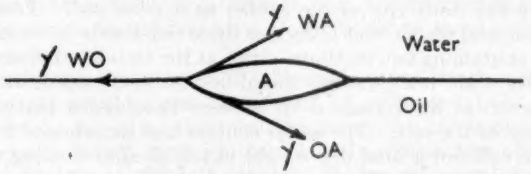


FIG. 1.

Consider a lens of the interfacial material (A) at the interface between the two phases, as shown in Figure 1. For the material to spread: $\gamma_{WO} > \gamma_{WA} + \gamma_{OA}$ (where γ_{WO} is the interfacial tension between water and oil phases, γ_{WA} between water and substance A and γ_{OA} between oil and substance A), and this is the condition that normally obtains when oil-water emulsion is stabilized. Now withdraw the aqueous phase, for example, by drying out. Oil now exists where water previously was, and the interfacial material (A) is no longer stable as a spread-out film, since the spreading force represented by γ_{WO} has been with-

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 25, No. 5, pages 334–345, February 1950.

drawn. Actually, stability of the emulsion is achieved by keeping γ_{WA} and γ_{OA} as small as possible. The hydrocarbon phase of rubber latex can be regarded as an oil phase, even though it is very much more viscous than the oil of most oil-water emulsions. In natural rubber latex γ_{WA} is determined by the polar side-chains of the protein molecule and γ_{OA} by the polypeptide backbone. That is, the protein has a fixed and particular orientation at the interface. When a soap is used as the emulsion stabilizer, the carboxylic group at the head of the molecule determines γ_{WA}, and because of its polar nature and consequent affinity for water molecules, γ_{WA} is very small. Similarly, γ_{OA} is determined by the long hydrocarbon chain of the soap, and is also low because of the affinity of the oil for similar hydrocarbon materials.

The withdrawal of most of the aqueous phase from latex by evaporation would leave an unstable condition unless the orientation of the interfacial material changed. This it undoubtedly does by a process allied to phase inversion, the final stages of drying out being equivalent to removal of water from a water-in-oil emulsion, the water having to diffuse through the hydrocarbon material.

With soap molecules reorientation is relatively easy, the polar heads remaining in the aqueous phase, now the disperse phase, and the hydrocarbon chains forming a hydrophobic outer surface to the globules of the disperse phase. With protein this reorientation would not be so easily accomplished, but there would be a tendency for the molecule to be no longer extended two-dimensionally at an interface, but coiled up with a majority of polar groups inside the coiled configuration. If the protein is replaced by saponin, strong evidence can be obtained for this explanation. At any stage during the drying-out process until less than 1 per cent of water remains, the partially dried rubber film can be redispersed by soaking in water[6]. When only about 1 percent of water remains, there comes a sharp end-point to attempted redispersion, and it is at this point that we may assume that the saponin molecules have orientated themselves to form the water-in-oil type of configuration.

A quite usual way of distinguishing oil-in-water from water-in-oil emulsions is by electrical conductivity. If a process allied to phase inversion does occur, as is suggested by the experiment reported with saponin, we should expect a sudden jump in the resistivity of the rubber as it dried out. To test this, a sample of commercial 60 per cent latex was dried out slowly in a small shallow ebonite trough containing two platinum strips at the ends as current electrodes. The conductivity of the latex was calculated from measurements, with a Lindemann electrometer, of the voltage drop between two further platinum strips, nearer the center of the cell. The water content was determined by repeated weighing of the cell and a final dry weight obtained after heating the rubber alone to 80° C for 3 hours. The results are plotted in the diagram, Figure 2, and show the expected form.

If this is a true explanation of what occurs in the drying out of latices, then certain information can be deduced as to the structure of the dried-out film, and from this probable structure properties deduced which would be expected to differ from a film vulcanized after drying. This paper is concerned with the discussion of the structure of the film, and presents data in support of the theory advanced.

Structure of films of dried vulcanized latex.—The cement theory of the film structure was disproved also by an experiment in which latex was recreamed four times in the presence of a soap, sodium laurate, to displace the protein layer. Other workers[7] have examined the validity of this procedure, and have shown

that the nitrogen in the dried film is reduced to about 0.02 per cent. This recreamed latex was then vulcanized, using sodium diethyldithiocarbamate as the accelerator and a proprietary dispersing agent, Dispersol L, which is alcohol-soluble. The absence of casein stabilizer and the like meant that some coagulation occurred during the vulcanizing process, and the yield was less than 100 per cent (usually about 90 per cent). This vulcanized latex was strained free from coagulum and dried out on levelled glass plates. Drying, which was at room temperature only, took place over two weeks. The use of heat was avoided in order that there should be no question of residual sulfur or accelerator causing vulcanization after the bulk of the water had been removed. When

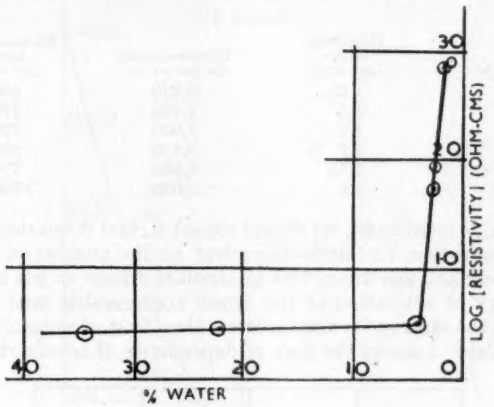


FIG. 2.

drying was apparently complete, the film was examined and had a strength similar to a normal vulcanized latex film. To add weight to the evidence, however, the soap was extracted from a second sample by refluxing with alcohol for 2 hours. This film was finally dried for a week at room temperature. This film also was indistinguishable in strength from a vulcanized latex film prepared in the usual way, although the amount of cement material present must have been extremely small.

It is considered, therefore, that cohesion between the particles must be by conventional chemical means, *i.e.*, either by primary-valence bonds linking rubber molecules directly, or the socalled secondary bonds or van der Waals' forces between adjacent rubber molecules. The imbibition of a solvent by a high polymer results in the destruction of the secondary valence bonds in the same way, and for the same reason, that solution of low molecular weight materials occurs. It is thus possible to distinguish between networks composed of primary valencies and those composed of secondary valencies by swelling in a good swelling agent and testing if the resultant mass can resist extension or shear. Films of dried vulcanized latex were swollen in benzene and showed the usual well-defined swelling maxima, thus indicating that the rubber molecules were sufficiently cross-linked to prevent dissolution, but the resultant mass could not be extended by any measurable amount and, although it could resist a very small shearing deformation, it collapsed into a mass of very small separate particles when larger shearing forces were applied. It is obvious from this experiment that primary-valency links do not exist between the particles, but

do exist within the particles. Cohesion between particles in the dried-out film exists by virtue of the van der Waals' forces between the molecules composing the outer surface of the particles. The swelling in benzene is limited because the cross-linking within the particle limits the total solvent uptake, but the imbibition neutralizes the secondary valencies and no cohesion can then exist between particles. The swollen mass cannot be extended because of lack of cohesion, but it resists very small shearing loads for the same reasons that a pile of stacked shot cannot easily be pushed over.

Properties of dried vulcanized latex.—Certain interesting consequences can be deduced from the above. If the most commonly discussed property, that of

TABLE 1

Sample	Combined sulfur (per cent)	Tensile strength (lb. per sq. in.)	Elongation at break (per cent)
A	1.05	2,210	830
C	1.5	2,250	770
D	1.7	1,940	790
G	1.7	2,440	830
E	1.75	1,980	710
F	1.8	2,000	700

tensile strength, is considered, we should expect to find it less dependent on the degree of vulcanization, *i.e.*, little dependent on the number of cross-links inside the particles; and less dependent in absolute values on the temperature of test (*i.e.*, energy of activation of the bonds concerned is less), although the actual value of the strength is always lower than that of vulcanized films from dry rubber. Table 1 shows the lack of dependence of tensile strength on the

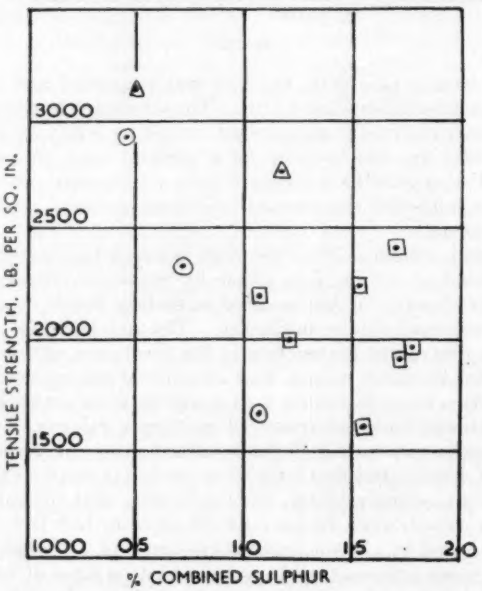


FIG. 3.—△ Commercial samples of vulcanized latex. ⊡ Taken from Table 1. ⊙ Other data obtained during this investigation.

combined sulfur for a series of vulcanized latices prepared at the same time under conditions which were as similar as possible, since all compounds were placed in beakers in an autoclave of the open-steam pan type at the same time, and vulcanized with a 15-minutes' rise at 20 lb. per sq. in. steam pressure (125° C), followed by 15 minutes at that temperature, and a period of cooling before opening the autoclave. The compounds differed only in the amounts of sulfur dispersion added to them.

The coefficient of variation of the tensile strength values is 8 per cent, which is not unreasonable for variations between tests carried out at different times

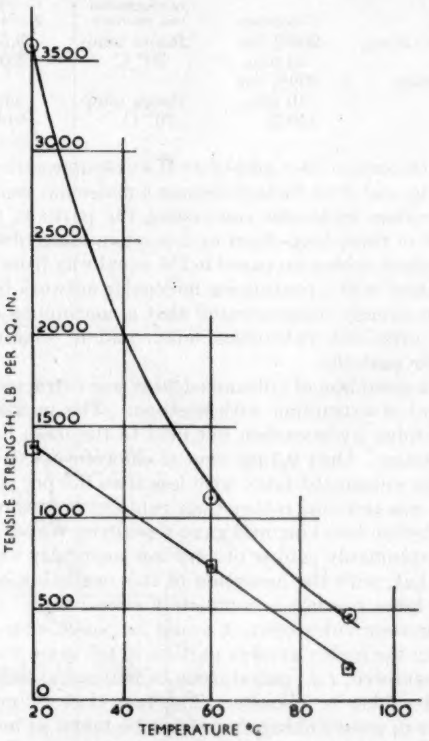


FIG. 4.—⊙ Vulcanized after drying out the latex. ⊡ Vulcanized as latex.

on materials whose compounding (*i.e.*, sulfur content) differs somewhat. However, if with the figures given in Table 1 are included other data obtained during this investigation, it might be held that there is a slight trend of values. This is illustrated by the scatter diagram given as Figure 3.

The effect of temperature on the tensile strength is shown in Figure 4. It may be presumed that at some more elevated temperature the tensile strengths become indistinguishable.

Attempts to determine the comparative tension set at elevated temperatures (70° C) failed because, even at 150 per cent elongation (less than one-fifth of the elongation at break at room temperature), vulcanized latex films broke

before they had been held extended for 10 minutes. Nevertheless, some comparative figures of tension set are shown in Table 2.

The bearing of these comparative figures on our concept of the structure of the dried film of vulcanized latex is more properly discussed in a later section when we consider our finding in the light of the current theory of rubberlike elasticity.

TABLE 2

TENSION SET

Sample	Elongation	Temperature of elongation and recovery	Set after recovery for 2 min.	10 min.	30 min.
Vulcanized after drying	200% for 10 min.	Room temp.	3.5	1.0	1.0
		70° C	13.0	8.5	7.5
Vulcanized as latex	200% for 10 min.	Room temp.	5.5	4.5	2.5
	150%	70° C	Broke in extension		

Structure of the vulcanized latex particle.—If we assume a diameter of 1 micron for the latex particle, and if we further assume a molecular weight of 300,000 for the rubber hydrocarbon molecules comprising the particle, we calculate that there are about 10^6 of these long-chain hydrocarbon molecules in each particle. In a piece of vulcanized rubber prepared in the usual way from dry rubber, these long-chains are formed into a continuous molecular network by the vulcanizing process. We have already demonstrated that a continuous network does not exist in a film of dried-out vulcanized latex, and it remains to discuss the structure within the particle.

A sample from a dried film of vulcanized latex was extracted with chloroform after a short period of extraction with acetone. The purpose of this was to dissolve out any rubber hydrocarbon not held to the main bulk of the rubber by chemical cross-links. Only 0.3 per cent of chloroform extract was obtained, and 0.5 per cent for vulcanized latex with less than 0.5 per cent combined sulfur. The extract was resinous rather than rubbery in nature, but it could be extended slightly before breaking and gave a positive Weber color reaction for rubber, and was presumably rubber of very low molecular weight. It may be taken, therefore, that, with the exception of this negligibly small amount, the rubber within the latex particle is completely cross-linked. If an outer layer only of the particle were vulcanized, it would be possible for vulcanized molecules to diffuse from the highly swollen particle in the same way that other high molecular weight material, *e.g.*, polystyrene or polyisobutene, can be extracted from a vulcanized rubber or ebonite. The fact that all molecules within a particle participate in cross-linking should not be taken as indicating that vulcanization proceeds uniformly throughout the particle. To investigate the possibility that the frequency of cross-links became fewer towards the center of the particle, the swellings in benzene or two series of dried films as a function of the combined sulfur were compared together with some commercially prepared vulcanized latex. The latices from which the films were prepared were similarly compounded, but one was vulcanized in latex form and the other vulcanized after drying out. The swelling in benzene as a percentage volume increase is shown in Figure 5, plotted against combined sulfur determined after acetone extraction. With 1 per cent or more of combined sulfur, the rubbers are indistinguishable, but with less than this, the rubber vulcanized after drying latex shows a distinctly higher swelling. This could arise for the following reasons.

(1) If the efficiency of the vulcanization reaction (number of cross-links formed per gram-atom of sulfur combined) were greater when the vulcanization is carried out with the rubber in latex form than when the rubber is dry.

(2) If vulcanization tended to occur more readily nearer the surface than in the center of the particle, due either to the slowness of diffusion of sulfur, accelerator, or other essential reagent or to the efficiency of the reaction being greater at the surface.

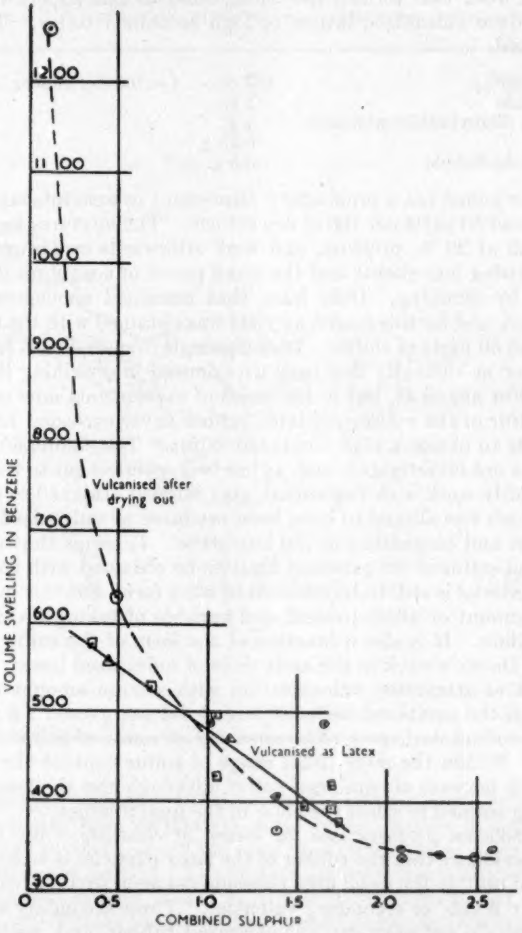


FIG. 5.—⊙ Vulcanized after drying out the latex. ⊡ Vulcanized as latex. △ Commercial vulcanized latex.

The fact that the effect is observed only with a combined sulfur of less than 1 per cent suggests that the first part of the second reason given above is the more probable cause of the phenomenon, although more data would be required

before it could be established. It is to be observed that this effect of lower swelling of vulcanized latex than of vulcanized dry rubber is not great, that rubber in the center of the particle is vulcanized, and that there is no question of a skin of more highly vulcanized rubber surrounding less highly or unvulcanized rubber. The data merely suggest that, with very small amounts of combined sulfur, the cross-links are not distributed with a uniform density throughout the particle.

Amount of combined sulfur and the color of the product.—In the course of the experimental work that formed the background to this paper, attempts were made to produce vulcanized latices of high combined sulfur. The following recipe was used.

Latex (60%)	167 cc.	(= 100 dry rubber content)
Zinc oxide	1 g.	
Sodium diethyldithiocarbamate	1 g.	
Casein	0.25 g.	
Sodium hydroxide	0.5 g.	

Sulfur was added (as a proprietary dispersion) in amounts equivalent to 2, 2.5, 3, 4, 10, and 50 parts per 100 of dry rubber. The mixtures were vulcanized in open steam at 20 lb. pressure, and were afterwards centrifuged to remove excess vulcanizing ingredients and the small pieces of coagulum that could not be removed by straining. Only latex that remained uncoagulated after 24 hours was used, and for this reason no yield was obtained with the mixtures containing 10 and 50 parts of sulfur. In compounds prepared with from 0.5 to 1.5 per cent sulfur no difficulty had been experienced in obtaining the amount of combined sulfur aimed at, but in the series of experiments now considered the combined sulfur of the vulcanized latex rubber never exceeded 1.8 per cent, in spite of efforts to obtain a high combined sulfur. The combined sulfur in the coagulum was not investigated, and, as has been pointed out to the authors[8], in some of the early work with vulcanized latex interest attached to the coagulum produced, which was alleged to have been produced as vulcanized latex of high sulfur content and coagulated in the autoclave. It seems that about 1.8 per cent combined sulfur is the practical limit to be obtained with the compounds used if the material is still to be retained in latex form, but this may be a function of the amount of alkali present and capable of taking up sulfur to form alkali polysulfide. It is also a function of the form of the sulfur, as is clearly indicated by Davey's work in the early days of vulcanized latex[9].

One effect of attempted vulcanization with a large amount of sulfur was that, although the combined sulfur obtained did not exceed 1.8 per cent, the color of the product darkened with increasing amounts of sulfur with which it was heated. Within the more usual range of sulfur content the color tended to darken with increase of combined sulfur, although also the temperature and time of drying seemed to affect the color of the final product.

Cohesion between particles and the theory of elasticity.—We have referred above to the evidence that the rubber of the latex particles is cross-linked in the usual way and that, in the dried film, cohesion between particles can be due only to the van der Waals' or secondary valencies. These secondary valence forces exist, of course, in ordinary dry unvulcanized rubber, and we have to make clear the distinction between the structure of unvulcanized dry rubber and dried vulcanized latex. In raw rubber we imagine a tangled mass of rubber hydrocarbon chains, most of which are held together only by virtue of their secondary valencies and entanglements. To remove a molecule from the mass, work has to be done only to overcome the secondary valence forces of that

molecule, provided the time taken to remove it is sufficiently long for the random Brownian movement of the chain arising from thermal motion to allow it to nullify any mechanical entanglement. To remove a molecule from the mass of a film of dried vulcanized latex, it would be necessary to overcome the primary-valence forces of the cross-linking atoms in addition to the secondary-valence forces. As an alternative to the removal of a single long-chain molecule from the film of vulcanized latex, consider the removal of a unit identifiable with the latex particle, for, as has been shown above, only secondary valencies have to be overcome. This involves the removal of an easily deformable mass containing some 10^6 molecules joined to each other by occasional cross-links.

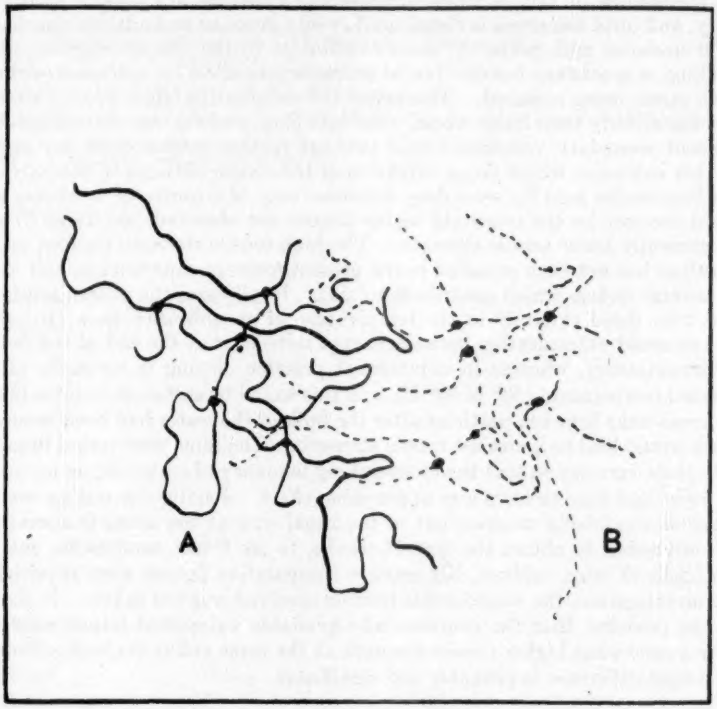


FIG. 6.

When considered in isolation, it will have a definite outline or envelope, as the secondary valencies tend to contact with similar masses having similar cohesive forces the envelope or outline loses its distinctness as it merges with the molecules of adjacent masses. The point is, perhaps, made clearer by Figure 6, where two adjacent masses, A and B, are shown in contact. It is difficult to distinguish to which mass the threadlike molecules belong (but one is shown in full line and one in dotted line—the lines representing the entangled threadlike molecules in the respective masses), although cross-links (shown by heavy dots where the chains cross; chains crossing without a heavy dot are not cross-linked) do not exist between the two masses, A and B, which are initially separated latex particles. It is easy to visualize from this diagram that, to separate the

particles the secondary valencies of a large number of rubber hydrocarbon chains must be overcome at the same time. An attempt to pull away one molecule results, through the action of the cross-linking, in an attempt to pull away very many, and it is this that distinguishes vulcanized latex films from dry unvulcanized rubber.

The stress-strain curve for dried vulcanized latex films, plotted with extension as the abscissa and stress as the ordinate, shows an initial part which is very flat, *i.e.*, the modulus is very low over the initial amount of extension; thereafter it rises fairly steeply to the breaking point. It may be thought that the initial low modulus is accounted for by readjustment under small stress of the boundaries of the particles. Secondary valencies are broken relatively easily, and until the stress is distributed evenly over the secondary valencies at the boundaries and, probably, some orientation of the chains occurred, some breaking of secondary bonds a few at a time would allow for extension without much stress being required. Thereafter the coöperative effect to which reference has already been made would come into play, and the cumulative effect of adjacent secondary valencies would prevent further extension at low stress. Further extension would be an extension of the elastic network of the particle. The boundaries held by secondary valencies only is a source of weakness and would account for the relatively higher tension set observed (see Table 2) and the generally lower tensile strength. The high tensile strength claimed in the literature has not been equalled in the present series of experiments, and there are several factors which contribute to this. In all cases the vulcanized latex films were dried carefully at the temperature of an unheated room (15° C or less) to avoid vulcanization by any reagent unreacted at the end of the period of vulcanization, whereas in commercial practice, drying is normally at an elevated temperature (60° to 80° C), and this would be sufficient to introduce a few cross-links between particles after the bulk of the water had been removed which would lead to increased tensile strength. The films were tested immediately they were dry so that the cross-linking tendency of oxygen in aging would not have had time to have any appreciable effect. Lastly, the testing was by means of dumbbells stamped out in the usual way at the usual temperature. It is advisable, to obtain the highest results, to use frozen samples for cutting dumbbells of latex rubbers, but as only comparative figures were required in this investigation, the considerable trouble involved was not taken. It should also be recorded that the commercially available vulcanized latices used did show a somewhat higher tensile strength at the same sulfur content, although the actual difference is probably not significant.

SUMMARY

A short theoretical introduction discusses the drying-out of emulsions and some data on electrical conductivity is presented showing that latex probably conforms to the general type. This is used as evidence against the theory that in dried-out films of vulcanized latex the particles are stuck together by the protein which initially surrounds the latex particle. Further experimental evidence concerns the suggestion that the van der Waals' or secondary valencies alone are responsible for the cohesion of the film. This proposed structure for the films is discussed in connection with their physical properties and in the light of modern theories of rubber elasticity.

ACKNOWLEDGMENTS

The authors acknowledge with thanks the advantage of discussion with I. Kemp, of Revertex Ltd., and G. Martin and W. G. Wren of the London Advisory Committee for Rubber Research (Ceylon and Malaya) before the work was commenced. Their thanks are also due to (Miss) J. B. Holtham for the sulfur determinations, to D. J. Hine for determinations of electrical conductivity, and to the Research Association of British Rubber Manufacturers for permission to publish this paper.

REFERENCES

[1] Schidrowitz, British patent 193,451 (Sept. 24, (1921)): 208,235 (Sept. 14, 1922)).
[2] Flint, "The Chemistry and Technology of Rubber Latex", London, 1938, p. 334.
[3] Hauser, "Latex", New York, 1930, p. 130.
[4] Von Weimarn, *Bull. Chem. Soc. Japan* **3**, 167 (1928).
[5] Van Dalfsen, *Arch. Rubbercultuur* **24**, 598 (1940).
[6] Martin, G., private communication.
[7] Baker, *Trans. Inst. Rubber Ind.* **16**, 165 (1940); Martin, *Proc. 2nd Rubber Technol. Conf.* (London), **1948**, p. 319.
[8] Stern, H. J. private communication.
[9] Davey, *J. Soc. Chem. Ind.* **42**, 473T (1923).

OXIDATION PROCESSES IN LATEX OF *HEVEA BRASILIENSIS* *

(Mrs.) L. N. S. de Haan–Homans

Indonesian Rubber Research Institute, Buitenzorg, Java

INTRODUCTION

To obtain a comprehensive and accurate understanding of the formation and functions of latex and rubber within the plant, it is necessary to carry the investigation of the enzymes of latex as far as possible. When the writer's experiments with the latex of *Hevea brasiliensis* were commenced, the oxidizing enzymes were selected as a starting point, because, of all the enzymes, these are the most frequently discussed in scientific literature dealing with latex and rubber. The blue discoloration which sometimes appears in latex, and frequently in latex coagulated with acid, is attributed to the action of oxidizing enzymes.

Peroxidase, oxidase, tyrosinase, and catalase are the oxidizing enzymes which are most frequently mentioned in scientific discussion as being present in latex, and reductase is also mentioned in connection with the oxidizing processes. Investigations were commenced by Spence[1] at the beginning of the century, and continued by others; one of the latest investigators was Bobilioff[2].

It was advisable, however, that modern methods should be brought to bear on the problem and that the investigations should be more extensive.

The experiments described in this paper were commenced during the Japanese occupation of Java, but it was not possible at that time to bring them to fruition because conditions generally were so unfavorable. It is hoped to continue this work in the near future.

THE ENZYMES INVESTIGATED AND THE METHODS USED

Catalase.—This enzyme liberates oxygen from hydrogen peroxide. Its activity can be measured simply by measuring the liberated quantity of oxygen from a given quantity of hydrogen peroxide.

Oxidases oxidize their substrates with the aid of molecular oxygen or, more properly expressed, they transfer hydrogen from their substrates to molecular oxygen, thus forming hydrogen peroxide.

There are several kinds of oxidases, all of which are more or less specific. Tyrosinase belongs to this class. The enzyme referred to by Spence and other investigators as oxidase must have been a polyphenol oxidase, most probably laccase. But until there is definite information, this enzyme will be referred to by the indeterminate title of oxidase.

Tyrosinase oxidizes monophenols, *e.g.*, tyrosine. The activity of the tyrosinase was measured by the Hammerich method[3], *i.e.*, by mixing the liquid containing the tyrosinase with a known tyrosine solution, and then conducting air through the mixture. The oxidation of the tyrosine by the tyrosinase produces a red color and afterwards a black precipitate. After a given time a sample is

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 25, No. 5, pages 346–363, February 1950.

taken and the tyrosine content determined. The amount of oxidized tyrosine is a measure of the activity of the tyrosinase.

The experiments were carried out at room temperature in the tropics (27 to 28° C).

Oxidase.—The first experiments on the oxidase of latex were carried out concurrently with peroxidase experiments by means of the Guthrie method[4]. Although useful, the results were not satisfactory. Later, futher experiments were made with the Barcroft-Warburg apparatus, in which the absorption of oxygen by the reaction mixture was measured. These experiments were conducted at a temperature of 30° C.

Peroxidase.—This enzyme, with the aid of hydrogen peroxide, oxidizes polyphenols to colored substances. The Guthrie method[4] was employed to determine the activity. This method is based on the principle that peroxidase in a solution of α-naphthol + paraphenylenediamine + hydrogen peroxide (pH 4.5) produces a purple indophenol stain. The amount of the stain produced within a given period is a measure ot the activity of the enzyme.

Reductase.—This enzyme is in the dehydrogenases group; it is able to transfer hydrogen from a donor to a suitable acceptor. Thus when air is excluded, methylene blue can be reduced to its colorless leucoform. It is noteworthy that this reduction can take place nonenzymatically if a substance with much lower redox-potential than methylene blue is present. The time taken to discolor the methylene blue solution, known as the reductase time, is a measure of the reductase activity.

All these enzymes thus have their own special substrates; they do not affect the rubber molecules.

THE SYSTEMS INVESTIGATED

In the course of the experiments, the enzyme activity of latex itself was investigated, together with its various parts, which included the white fraction, the yellow fraction[5], the serum obtained after coagulating latex or white fraction with formic acid, the water extract of the yellow fraction, the serum obtained by freezing latex or yellow fraction, and a variety of purified preparations of the sera and extracts. It is impossible to prepare serum by freezing white fraction, for the white fraction does not coagulate during freezing. On thawing, even after a week or ten days of freezing, the white fraction becomes more or less fluid again; in most cases it becomes a porridgelike lumpy mass, from which no serum separates. For purpose of convenience serum obtained by coagulation with acid will be referred to as serum-c, and that obtained by freezing as serum-f.

The latex used during the experiments was freshly harvested from regularly tapped trees, and in most cases was derived from different clones.

RESULTS

The investigations have shown that latex contains a complicated system of oxidizing enzymes, inhibitors, and powerful reducing agents, which exercise a mutual influence on one another. At times the experiments were hampered by these complications, which sometimes rendered the results confusing.

Catalase.—The investigation of the catalase[6] proved to be the least complicated of the experiments. When an adequate solution of hydrogen peroxide was added to fresh latex, oxygen was immediately released. Experiments with 5 grams of latex released 5 cc. oxygen in three minutes. Moreover, similar

results were obtained from a number of latices taken from different clones, a circumstance which is exceptional, because the activity of the other enzymes proved to be very variable with different latices.

In the course of these experiments the following points were observed. The catalase activity of the white fraction was only slightly less than it was for the whole latex, whereas that for the yellow fraction was much less, and amounted to only about one-third of the activity found for latex. Serum-c showed no catalase activity, which was in contrast to serum-f, which had a catalase activity equal to 40 to 75 per cent of that of the original latex. When ammonia was added to the latex (20 cc. of 20 per cent ammonia per liter of latex) the catalase activity diminished rapidly and was practically at zero within three days.

All the determinations of catalase activity were carried out at a pH of 6.5.

Tyrosinase.—When the tyrosinase experiments[6] were started, it was not known how strongly the enzymes in the latex were inhibited. The first impression was that there was no tyrosinase present, but when the experiments were prolonged to one day, which is beyond the few hours required for most of the known tests with tyrosinase, the presence of tyrosinase was revealed, and this was particularly evident when the yellow fraction was used.

It is noteworthy that although tyrosinase was always evident in the yellow fraction, which is a part of the latex, it was not always discovered in the latex itself, and it was never demonstrated in the white fraction.

In many tests on tyrosinase of other origin, described in the literature, the reaction is completed within a few hours, but when tests on the yellow fraction were made, the reaction often started only after 3 to 10 hours of conducting air through the reaction mixture, whereas the latex it was even later and slower. It would appear that some inhibitor, capable of being oxidized away when air is passed through the reaction mixture, is present with the tyrosinase, and that it is not until this inhibitor has been mostly eliminated that the tyrosinase can begin to act.

Some typical examples of reaction curves are shown in Figures 1 and 2.

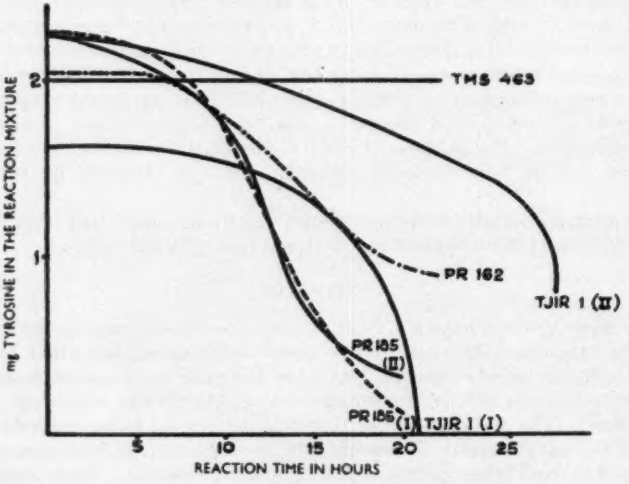


FIG. 1.—Tyrosinase activity. Reaction curves of latices of different clones.

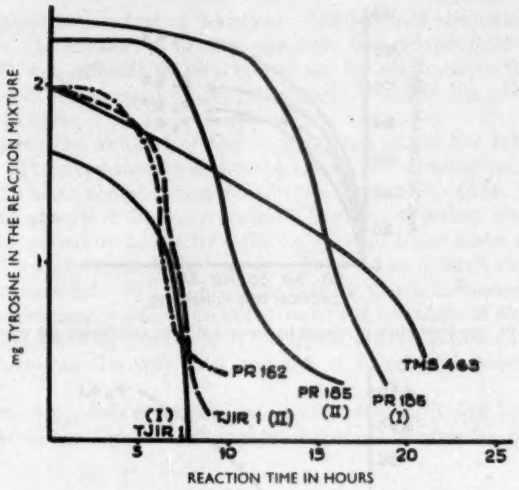


FIG. 2.—Tyrosinase activity. Reaction curves of yellow fractions, prepared from the latices reproduced in Figure 1.

When the latex is separated into a white and yellow fraction, the major part of the inhibitor remains in the white fraction. It might also be that the tyrosinase is bound to the yellow fraction. The tyrosinase can be extracted from the yellow fraction by means of water and then purified by precipitating the proteins with ammonium sulfate, and dissolving them again. When a purified preparation was examined by the Hammerich method[3], it showed great activity without an induction time.

The optimum pH, estimated for the purified preparation, appeared to be 7.7.

It was clear that much scope remains for further investigation of tyrosinase and its inhibitors. For instance, a few experiments were carried out with serum-f of both latex and the yellow fraction, by means of the Barcroft-Warburg apparatus, and during these experiments it was noted that the addition of tyrosine to the serum did not increase the oxygen absorption. It would, therefore, seem that further experiments with the purified preparations and the Warburg apparatus may give useful results.

Oxidase.—The preliminary experiments with the Guthrie method proved negative in almost all instances. It was only after purification that a weak activity could be discerned. This purification of preparations of serum-c of the latex and white fraction, and of serum-f of the latex and yellow fraction, was carried out by adding a five-fold quantity of alcohol to the serum, centrifuging off the precipitated proteins, and then dissolving them in water. The color produced in the Guthrie method, however, was always too faint to make possible a complete examination. Thus the question of whether the oxidase in the latex is truly inhibited or whether the reducing substances also present reduce the substrate again when it is oxidized by oxidase, thereby eliminating discoloration, reamined unanswered.

As latex is a rather unmanageable fluid, these experiments were almost invariably conducted with serum obtained by freezing latex or the yellow fraction.

Experiments with serum-c failed to show any absorption of oxygen.

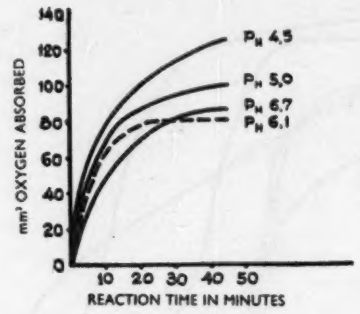


FIG. 3.—Absorption of oxygen by serum-f of latex at different pH values.

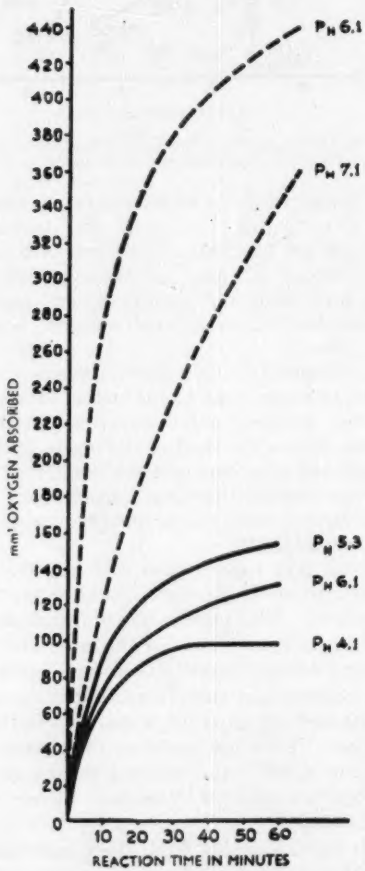


FIG. 4.—Absorption of oxygen by serum-f of latex at different pH values (the full drawn lines concern freshly thawed serum, the dotted lines the same serum after storing one day in a refrigerator).

It was clearly demonstrated, however, that serum-f absorbed oxygen at a faily high rate, the amount of oxygen absorbed being dependent on the pH of the serum. It was difficult to obtain average figures because there is such a great variation in the amount of oxygen absorbed, and in the pH at which the absorption is fastest.

In considering the amount of the oxygen absorption, the following points are relevant. The experiments do not do more than measure part of the process, because the latex absorbs oxygen from the moment it exudes from the tree. It continues to absorb it during transport, freezing, thawing, and throughout the intervening period up to the time the experiment takes place. At the commencement of an experiment the serum is exposed as a large surface and the temperature is raised to 30°. These are factors which influence the reaction rate. At the commencement of an experiment the quantity of oxygen that has already been absorbed by the serum is unknown, although this may be a potent factor in influencing the rate and amount of oxygen absorbed during the experiment.

If the foregoing points are taken into consideration, it will be realized that the differences in the rate of absorption of oxygen cannot be completely at-

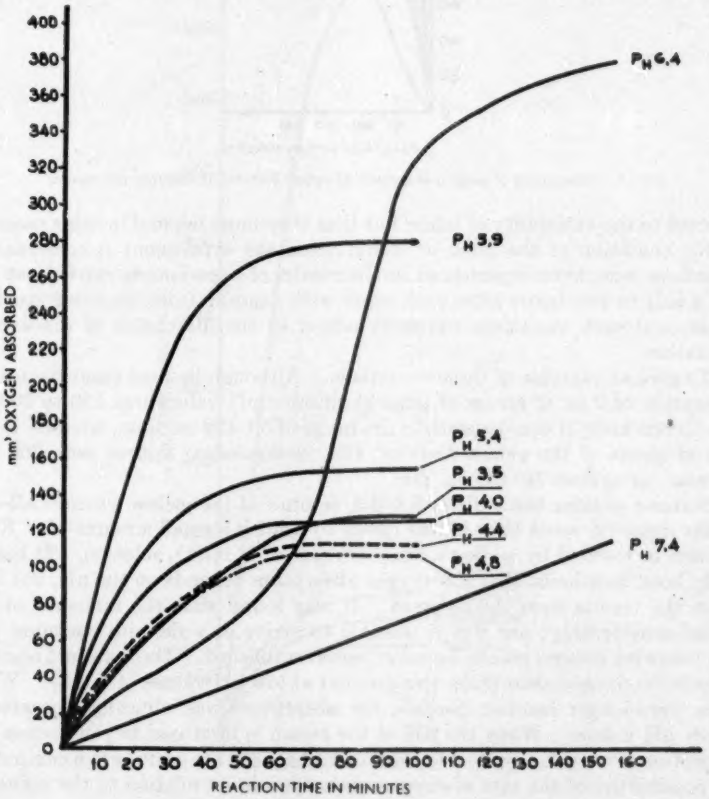


FIG. 5.—Absorption of oxygen by serum-f of yellow fraction at different pH values.

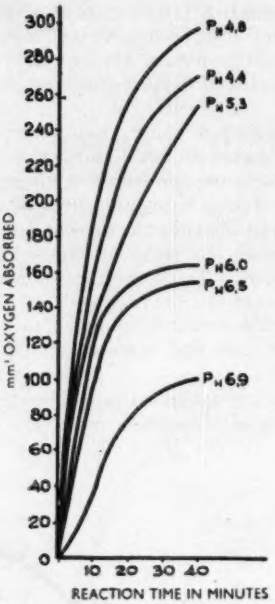


FIG. 6.—Absorption of oxygen of serum-f of yellow fraction at different pH values.

tributed to the variability of latex; but that they must depend in some measure on the condition of the latex or serum when the experiment is commenced. Variations were even experienced in the results of experiments carried out one and a half to two hours after each other with samples from the same stock of serum, and such variations naturally added to the difficulties of the experimentation.

To give an example of these variations. Although in most cases the rate of absorption of 2 cc. of serum of latex at suitable pH values was 150 to 200 cu. mm. in one hour, it could absorb in the range of 50–420 cu. mm., whereas in the case of serum of the yellow fraction, the corresponding figures were 200–350 cu. mm., as against 50–450 cu. mm.

Serum-f of latex has a pH of 6.0–6.3, serum-f of the yellow fraction 5.2–5.5. As the necessity arose the pH was raised by adding a small amount of *N* KOH solution or lowered by adding a small amount of *N* H_2SO_4 solution. It has already been mentioned that the oxygen absorption depends on the pH, but here again the results were inconsistent. It was found that the influence of pH varied considerably; nor was it possible to arrive at a definite optimum pH. The following general points, however, were established. During short reaction periods the oxygen absorption was greatest at low pH values (4.4–4.8). When there were longer reaction periods, the absorption was sometimes greater at higher pH values. When the pH of the serum is increased beyond seven the absorption of oxygen rapidly decreases. Figures 3–6 are useful when computing the possibilities of the rate of oxygen absorption in its relation to the influence of pH.

In the course of the experiments it was found that the absorption of oxygen by serum-f of latex was not due to the action of an oxidase, and that the absorption by serum-f of the yellow fraction was only partly due to an oxidase.

The following phenomena go to prove this. Flasks completely filled with serum, and closed with a stopper to prevent the serum from coming in contact with the air, were heated for 15–90 minutes to temperatures of from 50–70° C. Hereafter the serum was investigated in the usual way at 30° C, and it was found that its power to take up oxygen was considerably increased. If heated to temperatures of 80–100° C prior to the investigation, the absorption of oxygen was found to diminish but even after heating 90 minutes at 90° C or 30 minutes at 100° C, the absorption of oxygen still remained considerable. This cannot be expected with an enzyme. It should be stressed, however, that heating the serum was carried out in the absence of air; the power to absorb oxygen was lost within a minute when the serum was boiled in an open vessel.

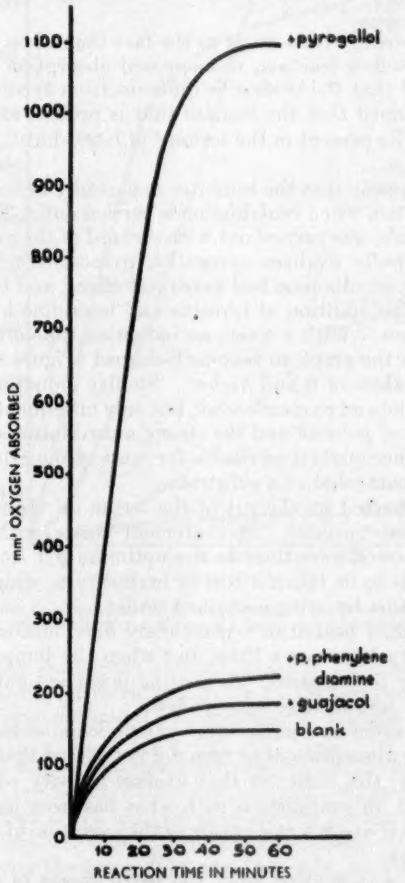


FIG. 7.—Absorption of oxygen of serum-f of yellow fraction (pH 5.5) with different substrates.

When potassium cyanide was added in a quantity sufficient to stop all enzyme action (0.4 cc. of a 0.5 per cent KCN solution to 2 cc. of serum) the power of absorption of oxygen by serum-f of latex was not decreased; in fact it is possible it was slightly increased.

When serum-f of the yellow fraction was treated in a similar manner with potassium cyanide, the results showed a partial decrease in oxygen absorption.

When a substrate for oxidases such as pyrogallol, *p*-cresol, and pyrocatechol was added to serum-f of latex, the oxygen absorption was not increased.

When similar substrates were added to serum-f of the yellow fraction, a considerable increase was recorded.

The foregoing leads to the conclusions: (1) that the absorption of oxygen by serum-f of latex is caused by some nonenzymatical component of the latex which can be activated or brought into existence by heating the serum to a maximum temperature of 70° C; (2) that the absorption of oxygen by serum-f of yellow fraction is partly caused by the same agent and partly by some oxidase.

Reference has already been made to the fact that when tyrosine was added to serum-f of the yellow fraction, no increased absorption took place. From this it is concluded that the oxidase is different from tyrosinase.

It must be assumed that the oxidase that is present in the serum-f of the yellow fraction is also present in the serum-f of latex, but that in the latter it is completely inhibited.

It would also appear that the inhibitor is partially or completely separated into the white fraction when centrifuging is carried out. The further study of the oxidase, therefore, was carried out with serum-f of the yellow fraction.

The oxidase rapidly oxidizes pyrogallol, pyrocathechol and *p*-cresol; the addition of *p*-phenylenediamine had much less effect, and that of guaiacol still less (Figure 7). The addition of tyrosine and benzidine had no effect on the absorption of oxygen. With *p*-cresol an induction time often occurred, which caused the curve in the graph to become S-shaped (Figure 8). This happened especially at pH values of 6 and higher. Similar induction effects were produced with pyrogallol and pyrocathechol, but only infrequently. The induction time characteristic of *p*-cresol and the strong autoxidation of pyrogallol at pH values of 6 and higher made it advisable for most of the experiments to be carried out with pyrocathechol as a substrate.

The influence exerted by the pH of the serum on the rate of oxidation of pyrocatechol proved variable. Measurement made with sera of different yellow fractions showed variations in the optimum pH from 4.5 to 6.5. For exact measurements to be taken it will be necessary to eliminate the unknown and interfering factors by using a purified serum.

When the serum is heated in a completely filled enclosed vessel at 50° or 60°, oxidase activity increases a little, but when the temperature is raised to 65° to 70°, activity is decreased. If heating is carried out for 30 minutes at 70°, there is hardly any oxidase activity left.

When pyrocathechol and potassium cyanide were added to serum-f of the yellow fraction, the absorption of oxygen did not exceed that of the serum without these additions; this indicates that oxidase activity was inhibited by the cyanide. This fact, in conjunction with what has been learned from heating the serum, confirms the enzymatic nature of the oxidation of added pyrocatechol and other substrates.

Peroxidase.—It was evident from the early stages of the work that the peroxidase in latex was also strongly inhibited. Investigating fresh latex by

the Guthrie method seldom showed positive reactions, but with serum-c of latex the results were nearly always positive. Serum-c of the white fraction, however, always gave a negative reaction.

The reaction of the yellow fraction was nearly always positive, and when experiments were made with extracts of the yellow fraction the peroxidase reaction was always positive and was stronger than that obtained with the original yellow fraction.

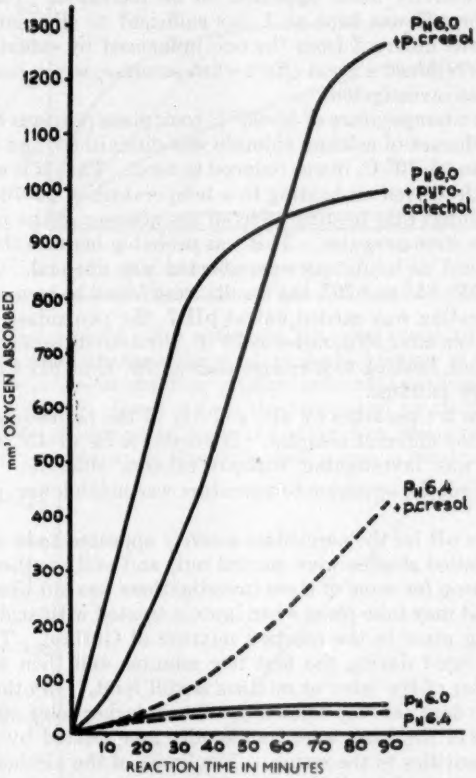


FIG. 8.—Absorption of oxygen by serum-f of yellow fraction pH 6.0 and pH 6.4 without any addition and after addition of *p*-cresol and pyrocathechol.

In most cases the peroxidase activity could be considerably increased by adding a small quantity of calcium chloride to the reaction mixture; such an influence, however, was not exerted by magnesium chloride or magnesium ammonium chloride.

The influence of calcium choride was variable, with a range of activation of the peroxidase from zero to more than 300 per cent. When the serum or extract was purified, the effect of the calcium chloride was decreased.

From this it is deduced that calcium chloride eliminated, partially or completely, an inhibitor of the peroxidase, and that this same inhibitor can be also partially removed by the purification process. It was also possible to partially

eliminate this inhibitor by means of filtration with a Seitz or Chamberland bacteria filter.

The presence of a second inhibitor of the peroxidase was also discovered. The pH of the strongly buffered mixture of Guthrie[4] is 4.5, and generally the pH of serum-c is also 4.5. When serum-c is added to the mixture, a certain peroxidase activity is found. When, however, the pH of a sample of the same stock of serum-c is raised to pH 7 and then investigated as usual at a pH of 4.5, the peroxidase activity often appeared to be increased. The short period during which the pH was kept at 7 was sufficient to eliminate an inhibitor. This inhibitor was different from the one influenced by calcium chloride, for calcium chloride retained a great effect when serum-c, which had been brought to a pH of 7, was investigated.

If heating to a temperature of 50–60° C took place previous to investigation at 30° C, the influence of calcium chloride was diminished, and if the temperature was raised to 65–70° C, it was reduced to zero. Thus it is established that the inhibitor is destroyed on heating to a temperature of 65–70° C.

It was also found that heating affected the activity of the peroxidase. At 50° C the results were irregular. This was probably because the rate at which the peroxidase and its inhibitors were affected was unequal. At higher temperatures, *e.g.*, 60°, 65° and 70°, the results were found to be more regular.

When the heating was carried out at pH 7, the peroxidase activity slowly decreased, but even after 90 minutes at 70° C, the activity was still rather great. On the other hand, heating to a temperature of 70° C at pH 4.5 destroyed the enzyme within 20 minutes.

The optimum temperature for the activity of the peroxidase showed small variations with the different samples. It proved to be 40–45° when the serum or preparation was investigated without calcium chloride. When calcium chloride was added, the optimum temperature was much lower, probably below 30° C.

The optimum pH for the peroxidase activity appeared to be 4.5. At a later period more detailed studies were carried out, and still another inhibitor was found. The reason for some of these investigations was our observation of the discoloration that may take place when latex is treated with acid and of the discoloration taking place in the reaction mixture of Guthrie. These discolorations often are rapid during the first few minutes and then suddenly cease, although the color of the latex or mixture is still faint. In other cases, where the discoloration does not stop suddenly, a much darker color may be obtained.

The proteins of the latex were fractionally precipitated by adding alcohol in increasing quantities to the serum. The limits of the alcohol concentration in the serum were used to distinguish the various fractions. Thus the first fraction, precipitated by the addition of alcohol to a concentration of 32 per cent (1 part alcohol 96 per cent, to 2 parts serum), was called fraction 0/32 or f 0/32. The investigation was mostly carried out on the fractions 0/32, 32/48 and 48/64.

Peroxidase activity occurring in fractions precipitated with alcohol concentrations higher than 64 per cent was negligible. Measurements of the amount of indophenol stain produced by the various fractions were taken after reaction periods of, respectively, 1, 2, 4, 6, 8, and 10 minutes.

The plotted results show clearly that the reaction curve of the fractions 0/32 and 32/48 were strongly deflected after a reaction period of 2–4 minutes, and that the curve of the fraction 48/64 was less deflected and often almost a straight line. A typical example appears in Figure 9. This example clearly

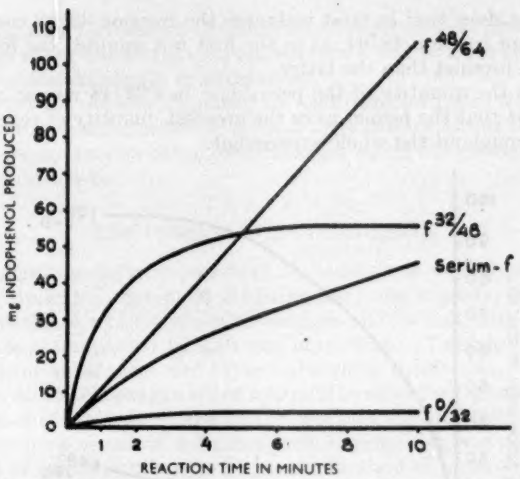


FIG. 9.—Peroxidase activities of serum-f of latex and of preparations therefrom.

demonstrated that the inhibitor acting in the reaction mixture with fraction 0/32 and 32/48 is not the reaction product itself, because in the mixture with fraction 48/64 much more reaction product is formed without interfering with the reaction. The difference between the amount of reaction product formed by fraction 48/64 as compared with the other two fractions was sometimes much greater than is shown in Figure 9; such a case is illustrated in Figure 10.

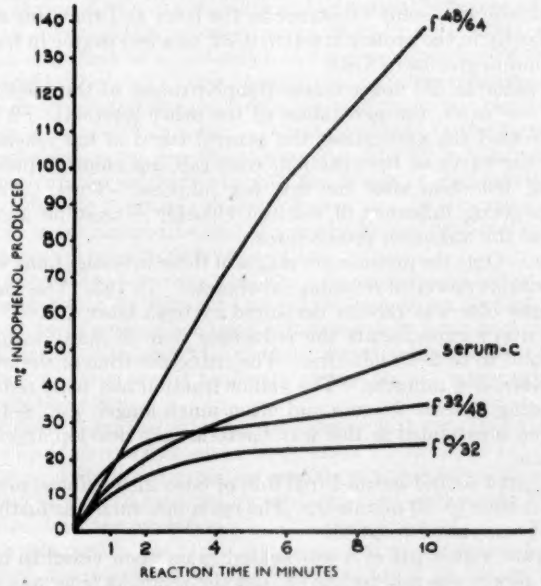


FIG. 10.—Peroxidase activities of serum-c of latex and of preparations therefrom.

The results show that in most instances the fraction 32/48 contained more peroxidase than fraction 48/64, as in the first few minutes the former formed more reaction product than the latter.

Sometimes the quantity of the peroxidase in f 32/48 was so much greater than in f 48/64 that the former gave the greatest quantity of reaction product Figure 11) throughout the whole experiment.

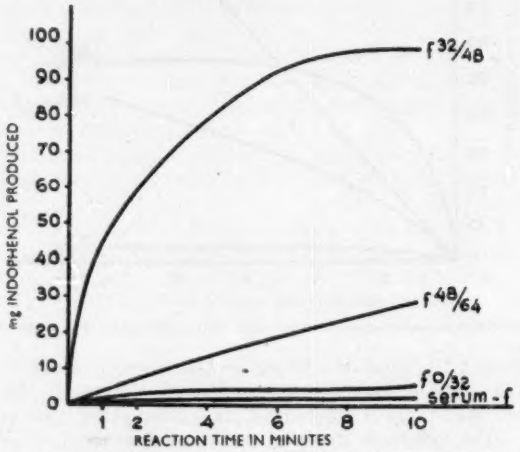


FIG. 11.—Peroxidase activities of serum-f of latex and of preparations therefrom.

The explanation may be that an inhibitor is formed by the reaction product of the peroxidase with some substance in the latex and that this substance accumulates mostly in the protein fraction 0/32, to a less degree in fraction 32/48, and to a minor degree in f 48/64.

Calcium chloride did not activate the peroxidase of the fraction 48/64, or except in a few cases, the peroxidase of the other fractions. Where calcium chloride activated the peroxidase, the general trend of the reaction remained unchanged; the curve of the reaction, with calcium chloride present, showed also a strong deflection after the first few minutes. Thus, it becomes clear that the activating influence of calcium chloride cannot be ascribed to the elimination of the unknown proinhibitor.

Reductase.—Only the preliminary stages of these investigations were possible.

Latex contains powerful reducing substances. In 1937, Van Dalfsen[7] found that methylene blue was rapidly decolored by fresh latex.

In the writer's experiments the reductase time of many samples of fresh latex was found to be 2–20 minutes. The reductase time of the white fraction was still shorter, 2–6 minutes. The yellow fraction had little reducing power, the period being at least 2 hours and often much longer, *e.g.*, 8–10 hours, but when the time is extended in this way bacteria may develop and influence the reductase time.

Serum-c (pH 4.5) and serum-f (pH 6.2) of latex also reduced methylene blue in a very short time (5–30 minutes). The reductase time was further shortened when the pH was raised to pH 8.

When serum with a pH of 8 was heated in an open vessel to boiling point, the reducing power was not destroyed, but the reducing time was prolonged to 30–300 minutes.

Calcium chloride had almost no influence on the reductase time. The short reductase time is not due to the enzyme reductase, but to some strongly reducing nonenzymatical substance or substances.

The decrease of the reducing power by heat does not prove that an enzyme is involved, as the reducing power after heating is still too strong for an enzyme. Moreover, there are several reducing substances which are strongly affected by heating, *e.g.*, vitamin C.

DISCUSSION AND CONCLUSION

The investigations have shown that, in addition to rubber particles, latex contains a complicated system of oxidizing enzymes, namely, catalase, tyrosinase and peroxidase, at least one other oxidase, all of which, with the exception of catalase, are accompanied by different inhabitors. The latex also contains strongly reducing substances and oxygen absorbing substances.

The power to absorb oxygen is not common to all reducing substances of the latex. Serum-c of latex decolored methylene blue rapidly but, when investigated in a Warburg vessel, it did not absorb oxygen. It was also established when the pH of serum is raised to 8 the decoloration of methylene blue is accelerated and that the absorption of oxygen decreased considerably at pH values higher than 7.

In view of the extraordinary amounts of oxygen that are so rapidly absorbed by latex, the biochemical condition of latex must undergo rapid changes from the moment it exudes from the tree. To determine the condition of the latex as it is in the tree, it will be necessary to collect the latex without allowing it to come into contact with oxygen.

The complexity of the system renders it necessary to investigate the problems from all angles. As a consequence of the mutual influence of the various components an investigation of only one of them in an isolated and purified condition, can only lead to a one-sided and incomplete view of the reactions of the substances in the latex. It is possible that different chain reactions occur in the latex. In support of this the writer can confirm former observations that carbon dioxide is produced in latex. It was produced in the serum, not as a product of fermentation by microörganisms, but directly in the fresh latex as it leaves the tree. In the experiments with the Warburg apparatus the production of carbon dioxide went on for hours before any deterioration of the latex took place. It is not impossible that the production of carbon dioxide and the absorption of oxygen may have a connection.

It is also necessary, however, that the various components of the enzyme shall be investigated in an isolated and purified condition so that observation can be made as to how their behavior is influenced in latex and serum.

A great difficulty that occurs in all these investigations is the extreme variability of latex, which makes it necessary to investigate many samples before conclusions can be drawn.

Little is known about the reducing substances: it is very probable that some of the amino acids demonstrated to be in latex by Altman[8] belong to these. Glutathione, *e.g.*, with its SH-group, is capable of reducing substances immediately after they have been oxidized by oxidases, thus eliminating the discolorations associated with the oxidation.

As is often assumed in the literature, enzymatical action is indeed responsible for the dark discolorations which sometimes occur on the surface of fresh latex, and occur far more frequently and intensively on the surface of latex

acidified for coagulation. It is evident that the lowering of the pH to 4.5–5.0 promotes discoloration. The optimum pH of the peroxidase is 4.5; the oxidase for which the optimum pH in latex is between 4.5 and 6.5, can be very active at pH 4.5. The tyrosinase has its optimum activity at pH 7.7; at 4.5 it has only about 60 per cent of its optimum activity. It is probable that tyrosinase is more inhibited in latex than oxidase, as in serum-f of yellow fraction the oxidase was always active, whereas the tyrosinase was inactive. This was proved by the addition of suitable substrates; oxygen absorption did not increase when tyrosine was added. The peroxidase in latex is less inhibited than oxidase and tyrosinase. Calcium chloride promotes the discoloration of latex and of all the enzymes it activates only the peroxidase.

Therefore it is highly probable that the discoloration of latex, acidified or not, is caused primarily by the peroxidase and that the peroxidase obtains the necessary hydrogen peroxide from the reactions of the oxidase.

The frequently occurring phenomenon in which discoloration starts rapidly in the latex and stops suddenly while the discoloration is still faint is in accordance with the observation recorded in the reaction curves of the peroxidase.

The white fraction never discolors spontaneously or after acidification; this is in accordance with the results which showed that the enzymes in the white fraction, except the catalase, are strongly inhibited and that the reducing substances are accumulated in the white fraction.

In contrast to the white fraction, the yellow fraction, in which most of the enzymes are more or less uninhibited, discolored almost always, with more rapid discoloration when acid was employed. This phenomenon occurred with the yellow fraction, even when the original latex did not discolor at all.

It may, however, be possible that the natural substrates of the enzymes are more or less linked to the yellow fraction, making it impossible for the white fraction to discolor, even if the enzymes in it were free and active.

Summarizing, the occurrence of the discolorations on the surface of latex or acidified latex depends on the proportions of the enzymes and the inhibitors. When the inhibitors predominate, as is mostly the case, no discoloration takes place.

As already mentioned, there is much future scope for the investigation of the enzymes of latex. The results already obtained tempt one to surmise that the oxidizing enzymes play an important part in the formation of the rubber in the plant. Many syntheses, including some employed in the preparation of synthetic rubber, are carried out in a suitable redox system, with addition of hydrogen peroxide or some other strong oxidizing agent to start the chain of reactions, and the addition of reducing substances to stop the reactions.

The oxidizing enzymes of the latex, with their inhibitors and reducing substances, form a balanced redox system in which hydrogen peroxide can be formed by the oxidases and eliminated again by the peroxidase and the catalase.

These conditions seem very suitable for a synthesizing medium.

SUMMARY

The occurrence of catalase, tyrosinase, oxidase and peroxidase in latex of *Hevea brasiliensis* has been investigated. These enzymes are present in fresh latex. With the exception of catalase they are accompanied by inhibitors, some of which are powerful reducing substances, and by nonenzymatical oxygen-absorbing substances. Thus latex contains a complicated redox system. Several properties of the enzymes and some properties of the reducing substances were determined.

An explanation is given for the spontaneous blue discoloration which frequently appears on the surface of latex, and the possible significance of the results on the formation of the rubber in the tree is indicated.

REFERENCES

[1] Spence, *India Rubber J.* **35**, 683 (1908); **36**, 25 (1908); *Biochem. J.* **3**, 165, 351 (1908); "Lectures on Rubber", 1908, p. 193; Cayla, *J. Agr. Trop.* **1908**, p. 333; Gorter, *Teysmannia* **23**, 39 (1912); Eaton, Dept. Agr. Fed. Malay States Bull. No. **17** (1912); Whitby, *Kolloid-Z.* **12**, 147, 190 (1912); *India Rubber J.* **45**, 941 (1913); de Jong, *Mededeel. Agr. Laboratorium* X (1915); de Bries, *Arch. Rubbercultuur* **1917**, p. 178; Heuren and Heusser, *Arch. Rubbercultuur* **4**, 137A (1919–20).
[2] Bobiblioff, *Arch. Rubbercultuur* **5**, 95 (1921); **8**, 819 (1924).
[3] Hammerich, *Biochem.-Z.* **239**, 277 (1931).
[4] Guthrie, *J. Am. Chem. Soc.* **53**, 242 (1931).
[5] For the separation of latex into a white and a yellow fraction, see Homans and van Gils, *Proc. Rubber Technol. Conf.* (London), **1948**, p. 292.
[6] This work was carried out in coöperation with W. B. Deys, then of the Proefstation, West Java.
[7] Van Dalfsen, *Arch. Rubbercultuur* **21**, 1 (1937).
[8] Altman, *Arch. Rubbercultuur* **24**, 647 (1940).

VULCANIZATION OF NEOPRENE TYPE W *

D. B. FORMAN, R. R. RADCLIFF, AND L. R. MAYO

RUBBER LABORATORY, E. I. DU PONT DE NEMOURS & COMPANY, INC., WILMINGTON, DELAWARE

The first general purpose type of chloroprene (2-chloro-1,3-butadiene) polymer (Duprene-D) was manufactured in 1932 by means of a mass polymerization method[1]. The development of emulsion polymerization techniques made possible the introduction in 1935 of a second type of chloroprene polymer (Neoprene Type E); in 1938 a third fundamental change in polymerization methods resulted in a faster curing elastomer, Neoprene Type G. Since that time, several modifications of this latter class of polymer have been produced commerically, notably Neoprene Types GN, GN-A, and RT—none of which represents a fundamental departure from Type G.

More recently, considerable research effort on chloroprene polymerization has been directed toward the development of new polymers showing a minimum of change in plasticity, processability, or rate of vulcanization during long periods of storage. A consequence of this research has been a fourth basic class of chloroprene polymer, represented by Neoprene Type W. This improved polymer has a much more uniform molecular-weight distribution than any of the other Neoprenes and, in addition, contains no sulfur, thiuram disulfide, or other compound capable of decomposing to yield either free sulfur or a vulcanization accelerator.

In addition to possessing improved stability, this Neoprene has been observed to differ markedly from previous chloroprene polymers in many important respects. Perhaps the most striking difference is its unique response to various vulcanization techniques. This difference is believed to be due at least in part to a fundamental difference in polymer structure as well as the complete absence of thiuram disulfide and sulfur from the polymer.

The elastomer compounds discussed herein were prepared and tested according to procedures established by the American Society for Testing Materials. The following designations are applicable to the various tests.

Tests	A.S.T.M. designation
Modulus, tensile strength, and stress-strain	D 412–41
Compression set	D 395–47T (Method B)
Hardness	D 676–47T (Shore A Durometer)
Heat build-up	D 623–41T (Method A, $\frac{3}{16}$-inch stroke)
Resilience	D 945–48T

Where indicated, the tendency to scorch of the compounds was measured by means of the Mooney shearing disk viscometer operating at a temperature of 121.1° C (250° F), using the small rotor. The time to scorch was selected as the time for the Mooney viscosity to increase 20 units from the minimum value. When the viscosity had not increased by 20 units within a 35-minute period, the test was terminated.

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 42, No. 4, pages 686–691, April 1950.

The chloroprene polymers such as Neoprene Types E, GN, CG, and RT vulcanize satisfactorily with suitable combinations of metallic oxides[2]. The curing system most widely employed consists of a mixture of 5 parts of zinc oxide and 4 parts of extra-light calcined magnesium oxide. Table I and Figure 1 show a comparison of the physical properties of a Neoprene Type W and a conventional Neoprene Type GN compound, using this curing system, and clearly demonstrate its impracticability for this new polymer. The slow rate of

TABLE I

METALLIC OXIDE VULCANIZATION OF NEOPRENE TYPES GN AND W

Base compound	A-1	B-1
Neoprene Type W	100	..
Neoprene Type GN	..	100
Phenyl-α-naphthylamine	2	2
Extra light calcined magnesium oxide	4	4
SRF carbon black	29	29
Stearic acid	0.5	0.5
Zinc oxide	5	5
Cure (min. at 153° C)	Stress at 500% elongation (lb./sq. inch)	
10	250	2275
20	900	2550
40	1750	2800
	Tensile strength at break (lb./sq. inch)	
10	800	2850
20	1550	3075
40	2750	3225
	Elongation at break (%)	
10	1060	760
20	850	680
40	740	600
	Hardness	
10	51	59
20	52	59
40	53	61

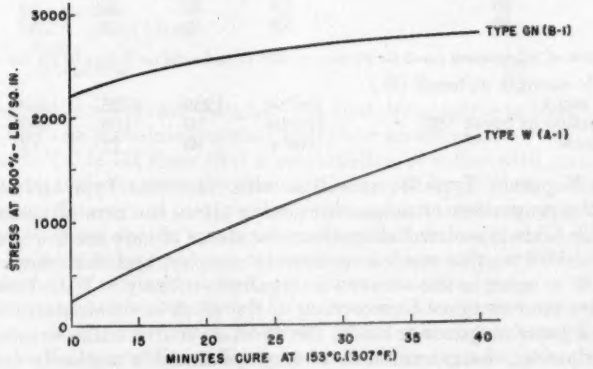


FIG. 1.—Vulcanization of Neoprene Types W and GN with oxides of zinc and magnesium.

curing and low state of cure obtained with the Type W compound, even after vulcanizing for 40 minutes at 153° C, show the need for a more active form of acceleration.

One of the ways to adjust rate of curing in Neoprene Type GN compounds is to vary the ratio of magnesium oxide to zinc oxide. Ordinarily, the lower the ratio, the more rapid the rate of cure[3]. Various concentrations of magnesium oxide were added to a Neoprene Type W base compound containing 5 parts of zinc oxide. The results are shown in Table II and Figure 2. The data show

TABLE II

EFFECT OF MAGNESIA CONCENTRATION ON VULCANIZATION OF NEOPRENE TYPE W

Base compound

Neoprene Type W	100
Phenyl-α-naphthylamine	2
SRF carbon black	29
Stearic acid	0.5
Zinc oxide	5

	A-2	B-2	C-2	D-2	E-2
% Extra-light calcined magnesium oxide added to base compound	0	1	2	4	10
Mooney scorch (min.)	10	34	45+	35+	45+
Cure (min. at 153° C)	Stress at 500% elongation (lb./sq. inch)				
10	1650	1350	300	250	250
20	1675	1550	1525	900	500
40	1750	1650	1650	1750	950
	Tensile strength at break (lb./sq. inch)				
10	3150	2400	825	800	850
20	3150	2425	2775	1550	1175
40	3175	2550	2825	2750	1675
	Elongation at break (%)				
10	820	740	1020	1060	1080
20	790	720	770	850	1000
40	780	680	730	740	840
	Hardness				
10	52	51	48	51	54
20	52	51	52	52	54
40	52	52	53	53	58
Properties of vulcanizates cured for 20 min. at 153° C, and aged for 7 days in 121° C air oven					
Tensile strength at break (lb./sq. inch)	Brittle	1200	1725	1850	1475
Elongation at break (%)	Brittle	90	180	180	120
Hardness	100+	85	72	72	73

that with Neoprene Type W, as well as with Neoprene Type GN compounds, varying the proportion of magnesium oxide alters the rate of curing. When magnesium oxide is omitted altogether, the states of cure are lower than desirable. In addition, this stock is extremely scorchy, and the resistance of the vulcanizate to aging in the air oven is impaired seriously. With 1 part magnesium oxide, the resistance to scorching of the stock is substantially improved; and with 2 parts magnesium oxide, the Mooney scorch value becomes greater than 45 minutes. Larger amounts of magnesium oxide markedly decrease the state of curing. Accordingly, the ratio of 2 parts of magnesium oxide to 5

parts of zinc oxide has been considered as optimum, and was used throughout the compounding studies which follow.

Since the state of cure obtained with magnesium and zinc oxides is undesirably low, the organic accelerators normally used by the rubber industry for natural rubber and GR-S were investigated next. The studies were made by applying conventional rubber compounding practices, *i.e.*, sulfur was used in

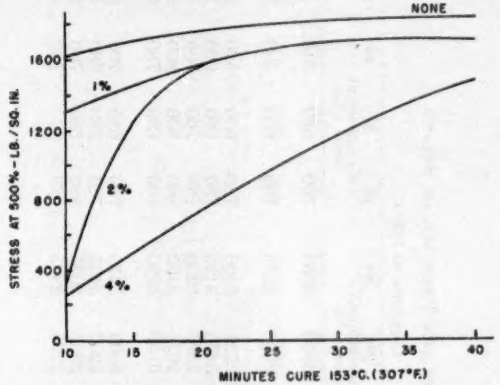


FIG. 2.—Effect of magnesium oxide concentration on vulcanization of Neoprene Type W in presence of zinc oxide.

conjunction with the accelerators. It was soon found that, with Neoprene Type W, the percentages of sulfur and accelerator required for vulcanization were generally less than those needed to vulcanize natural rubber.

Table III shows the stress-strain properties of vulcanizates containing various conventional accelerators in the following base compound, which was vulcanized in all cases at 153° C for the times indicated.

Base compound	
Neoprene Type W	100
Phenyl-α-naphthylamine	2
Stearic acid	0.5
Extra-light calcined magnesium oxide	2
Zinc oxide	5
SRF carbon black	29
Sulfur	1
Accelerator	0.5

For reference, two controls are included, one containing sulfur in the absence of accelerator, and one containing neither sulfur nor accelerator.

The data in Table III show that a combination of sulfur with many of the conventional organic accelerators vulcanizes Neoprene Type W very effectively. In several cases, the rates of curing among the various accelerators show differences similar to those shown by the same accelerators in natural-rubber vulcanizates. Notable exceptions are mercaptobenzothiazole and benzothiazolyl disulfide, which are relatively weak vulcanization accelerators in Neoprene Type W compounds, whereas they are reasonably strong in natural-rubber vulcanization. It is noteworthy, however, that both these chemicals act as accelerators in Neoprene Type W, because both are retarders in Neoprene Type GN. The effect of sulfur alone on the vulcanization of Neoprene Type

TABLE III

VULCANIZATION WITH VARIOUS ACCELERATORS IN THE PRESENCE OF SULFUR

Compound identification	Accelerator	Cure (min. at 153° C)											
		Stress at 500% (lb./sq. inch)			Tensile at break (lb./sq. inch)			Elongation at break (%)			Hardness		
		10	20	40	10	20	40	10	20	40	10	20	40
A-3	2-Mercaptothiazoline	2175	2400	2850	3575	3600	3550	760	670	610	58	58	58
B-3	Piperidinium pentamethylene-dithiocarbamate	2100	2750	3050	3200	3500	3275	760	620	540	52	56	58
C-3	Butyraldehyde-aniline condensation product	1150	2850	3025	2900	3725	3500	780	640	560	53	58	58
D-3	Diphenylguanidine	1650	2525	2975	2725	3475	3425	780	660	600	54	58	59
E-3	Zinc dimethyldithiocarbamate	2050	2150	2350	3150	3375	3200	780	760	700	52	53	53
F-3	Mercaptobenzothiazole	1370	1500	1875	2550	2675	3100	860	800	800	49	51	52
G-3	Benzothiazyl disulfide	1240	1625	2000	2675	3150	3200	860	880	780	52	52	53
H-3	Tetramethylthiuram monosulfide	1925	2200	2425	3100	3400	3475	780	680	700	53	53	53
I-3	Tetramethylthiuram disulfide	1975	2200	2375	3200	3200	3425	720	780	680	53	53	54
J-3	Control (sulfur only)	830	1825	2200	1825	2950	3025	880	740	700	52	52	54
K-3	Control (oxides only)	300	1525	1650	825	2775	2825	1020	770	730	48	52	35

TABLE IV

EFFECT OF VARIOUS ACCELERATORS IN THE ABSENCE OF SULFUR

Compound identification	Accelerator	Min. cured at 153° C											
		Stress at 500% (lb./sq. inch)			Tensile at break (lb./sq. inch)			Elongation at break (%)			Hardness		
		10	20	40	10	20	40	10	20	40	10	20	40
A-4	2-Mercaptothiazoline	1925	2200	2525	3450	3625	3560	770	690	670	55	56	57
B-4	Tetramethylthiuram monosulfide	1800	2075	2100	3400	3575	3250	800	780	700	52	53	53
C-4	Condensation products of butyraldehyde and aniline	540	1650	2525	1380	2675	3275	1000	710	600	49	52	54
D-4	Diphenylguanidine	420	750	1700	1060	1625	2875	980	940	700	49	51	53

W is of interest because it acts as a mild curing agent under these conditions. The solubility of sulfur in Neoprene Type W vulcanizates is low (less than 1 per cent) and visual observations have indicated that its rate of combination is slow; therefore, blooming may occur in unaccelerated stocks except on extended cures.

Since sulfur in the absence of organic accelerators has been shown to affect the state of cure of Neoprene Type W, the effect of several accelerators in the absence of sulfur was investigated. This was of particular interest since the accelerating effects of aldehyde, amine, and guanidine accelerators in Neoprene Type GN compounds containing magnesium and zinc oxides are well-known. Table IV shows such a comparison in the following base compound which was vulcanized at 153° C for the times indicated:

Base compound	
Neoprene Type W	100
Phenyl-α-naphthylamine	2
Stearic acid	0.5
Extra-light calcined magnesium oxide	2
Zinc oxide	5
SRF carbon black	29
Accelerator	0.5

The data in Table IV reveal several interesting and somewhat unexpected results. For example, diphenylguanidine and the condensation product of butyraldehyde and aniline are essentially ineffective in the absence of sulfur, while 2-mercaptothiazoline and tetramethylthiuram monosulfide are very effective

TABLE V

VULCANIZATION WITH 2-MERCAPTOTHIAZOLINE

Base compound				
	A-5	B-5	C-5	D-5
Neoprene Type W	100	100	100	100
Phenyl-α-naphthylamine	2	2	2	2
Stearic acid	0.5	0.5	0.5	0.5
Extra-light calcined magnesium oxide	2	2	2	2
SRF carbon black	29	29	29	29
Zinc oxide 1	5	5	5	5
2-Mercaptohiazoline	..	0.25	0.5	1
Mooney scorch (min.)	45+	45+	25	13
Cure (min. at 153° C)	Stress at 500% elongation (lb./sq. inch)			
10	300	1800	1925	2000
20	1525	2025	2200	2400
40	1650	2225	2525	2825
	Tensile strength at break (lb./sq. inch)			
10	825	3250	3450	3350
20	2775	3325	3625	3475
40	2825	3425	3650	3575
	Elongation at break (%)			
10	1020	730	770	760
20	770	725	690	720
40	730	660	670	670
	Hardness			
10	48	53	55	55
20	52	53	56	56
40	53	54	57	58

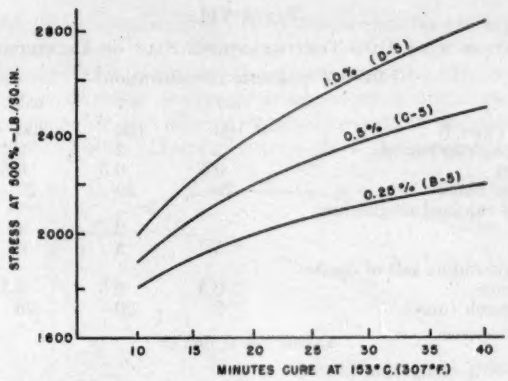


FIG. 3.—Vulcanization of Neoprene Type W with 2-mercaptothiazoline.

under these conditions. The latter observation is of considerable importance because it affords an opportunity to produce satisfactory Neoprene Type W vulcanizates in applications where the inclusion of even a small amount of sulfur would be undesirable.

TABLE VI

NONSULFUR VULCANIZATION OF NEOPRENE TYPES W AND GN

Base compound	A-6	B-6	C-6	D-6
Neoprene Type W	100	100	..	..
Neoprene Type GN	..	..	100	100
Phenyl-α-naphthylamine	2	2	2	2
Stearic acid	0.5	0.5	0.5	0.5
SRF carbon black	29	29	29	29
Extra-light calcined magnesium oxide	2	2	4	4
Zinc oxide	5	5	5	5
Di-o-tolylguanidine salt of dicatechol borate	0.5	..	..	0.5
4,4′-diaminodiphenylmethane	..	0.5	..	..
Mooney scorch (min.)	20	24	29	16
Cure (min. at 153° C)	Stress at 500% elongation (lb./sq. inch)			
10	2700	1725	2275	2650
20	2775	3175	2550	2900
40	2900	3350	2800	3050
	Tensile strength at break (lb./sq. inch)			
10	3300	2825	2850	3025
20	3200	3275	3075	3025
40	3200	3425	3225	3050
	Elongation at break (%)			
10	600	740	760	600
20	560	520	680	530
40	530	520	600	500
	Hardness			
10	57	53	59	62
20	57	57	59	63
40	58	57	61	63

TABLE VII

VULCANIZATION WITH DI-*o*-TOLYLGUANIDINE SALT OF DICATECHOL BORATE

(Effect of magnesia concentration)

	A-7	B-7	C-7	D-7
Neoprene Type W	100	100	100	100
Phenyl-α-naphthylamine	2	2	2	2
Stearic acid	0.5	0.5	0.5	0.5
SRF carbon black	29	29	29	29
Extra-light calcined magnesium oxide	..	2	4	10
Zinc oxide	5	5	5	5
Di-*o*-tolylguanidine salt of dicatechol borate	0.5	0.5	0.5	0.5
Mooney scorch (min.)	2	20	28	45
60-Min. cure at 108° C				
Stress at 500% elongation (lb./sq. inch)	2550	1110	550	280
Tensile strength at break (lb./sq. inch)	2725	1875	1280	900
Elongation at break (%)	540	800	860	1300
Hardness	56	52	52	53
Cure (min. at 153° C)	Stress at 500% elongation (lb./sq. inch)			
10	2625	2850	2600	1400
20	2600	2950	2950	1950
40	2550	3025	3250	2625
	Tensile strength at break (lb./sq. inch)			
10	2625	3325	3500	2450
20	2875	3150	3050	2750
40	2550	3350	3250	3000
	Elongation at break (%)			
10	500	580	640	800
20	560	560	520	660
40	500	540	500	560
	Hardness			
10	54	58	58	57
20	54	58	58	59
40	53	58	59	61

The data discussed thus far have involved a single concentration (0.5 part) of organic accelerator, with or without sulfur. Most vulcanization reactions involving natural rubber are influenced by the concentrations of accelerator. This is also true of Neoprene Type W, as illustrated by the data in Table V and Figure 3, in which the properties of a series of vulcanizates containing varying percentages of 2-mercaptothiazoline in the absence of sulfur are shown. As might be anticipated, the state of cure increases proportionately to the percentage accelerator added, although the processing safety becomes questionable when more than 0.5 part is used.

It is well known that materials such as the di-*o*-tolylguanidine salt of dicatechol borate and 4,4′-diaminodiphenylmethane exert a powerful accelerating effect on Neoprenes such as Types GN or RT, and are usually used when extremely fast cures are required. An investigation showed that these accelerators are also very effective in Neoprene Type W. The data are summarized in Table VI and conventional Neoprene Type GN vulcanizates with

and without the di-*o*-tolylguanidine salt of dicatechol borate are included for purposes of comparison.

Since the data in Table II showed the strong retarding effects of magnesium oxide in the absence of sulfur or organic accelerators, a similar comparison was made in the presence of the di-*o*-tolylguanidine salt of dicatechol borate, a strong accelerator. Table VII and Figure 4 show the results of this compari-

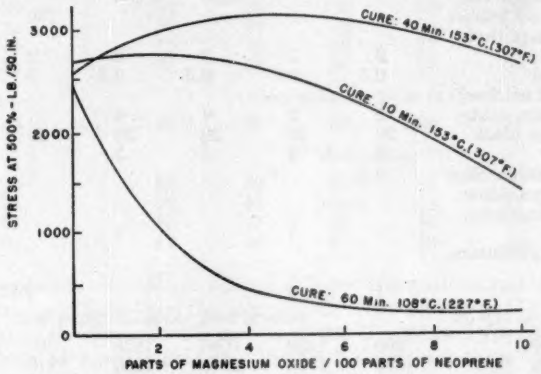


FIG. 4.—Effect of magnesium oxide concentration on vulcanization of a Neoprene Type W compound in presence of di-*o*-tolylguanidine salt of dicatechol borate.

son. The data show clearly that magnesium oxide also is very effective in the presence of an active accelerator. The addition of two parts magnesium oxide markedly increases the processing safety of the stock, as judged by either the Mooney scorch data or the physical properties of the vulcanizate cured at 108° C. Additional amounts further increase the processing safety of the stocks. The use of 10 parts magnesium oxide results in a decided undercure in the vulcanizates cured at 153° C, but this effect is not shown in the stocks containing either 2 or 4 parts. Since the processing safety of the stock containing 4 parts magnesium oxide appears to be great enough to ensure suitable factory operations, this amount appears to be the most desirable to use in Neoprene Type W stocks accelerated by the di-*o*-tolylguanidine salt of dicatechol borate.

A complete comparison of the physical properties of vulcanizates of Neoprene Type W with those of Neoprene Type GN or natural rubber is beyond the scope of this paper. However, the various methods of vulcanization of Neoprene Type W have so pronounced an effect on certain properties that comparisons with these elastomers are of interest. Two properties which are considered especially noteworthy in Neoprene Type W vulcanizates are the shape of the stress-strain curve and compression set, particularly at elevated temperatures. Table VIII shows comparisons of these properties of the 3 elastomers. With each elastomer, 2 compounds were selected; first, a compound which might be considered a representative general purpose or conventional type, and, secondly, a compound designed to enhance particularly the properties of compression set and resilience. Thus, in Table VIII compounds A-8, C-8, and E-8 represent the first type while B-8, D-8, and F-8 represent the second type.

With either type of compound a comparison of the stress-strain properties of Neoprene Type W with those of Neoprene Type GN or natural rubber shows that they are intermediate between these elastomers. Both of the Neoprene

TABLE VIII

PROPERTIES OF NEOPRENE TYPE W VULCANIZATES AND COMPARISON WITH NEOPRENE TYPE GN AND NATURAL RUBBER

	Base compound					
	A-8	B-8	C-8	D-8	E-8	F-8
Neoprene Type W	100	100	..	..	..	..
Neoprene Type GN	..	..	100	100	..	..
Smoked sheet rubber	..	..	..	..	100	100
Phenyl-α-naphthyl-amine	2	2	2	2	2	2
Stearic acid	0.5	0.5	0.5	0.5	3	1
Extra-light calcined magnesium oxide	2	2	4	4	..	..
SRF carbon black	29	29	29	29	39	39
Zinc oxide	5	5	5	5	5	5
2-Mercaptothiazoline	0.5	..	..	..	1	..
Di-o-tolylguanidine salt of dicatechol borate	..	1	..	1	..	..
Tetramethylthiuram disulfide	..	..	..	..	..	2
Sulfur	1	..	..	..	2.75	0.5
Cure (min. at 142° C)	Stress at 300% elongation (lb./sq. inch)					
10	690	1400	1060	1625	960	1400
20	890	1700	1250	1750	1210	1475
40	1180	1800	1410	1875	1425	1550
80	1410	1875	1600	2025	1550	1475
	Stress at 500% elongation (lb./sq. inch)					
10	1725	2825	1960	2525	2450	3325
20	2100	3300	2125	2625	2850	3350
40	2550	3300	2375	2850	3250	3550
80	2950	..	2600	..	3400	3350
	Tensile strength at break (lb./sq. inch)					
10	3100	3550	2550	2750	4200	4250
20	3250	3325	2800	2850	4600	4000
40	3250	3300	3175	2850	4550	4400
80	3400	3150	3025	2675	4050	4000
	Elongation at break (%)					
10	860	520	840	600	680	600
20	700	520	800	580	640	560
40	680	500	780	500	600	580
80	580	460	640	400	580	560
	Hardness					
10	52	58	58	62	62	57
20	53	58	59	62	58	57
40	53	58	61	62	58	57
80	57	59	61	63	58	57
	Resilience (%)					
10	67	76	76	81	82	85
20	69	76	76	81	84	85
40	71	77	77	81	84	85
80	76	77	79	82	83	85
	Compression set (22 hr. at 70° C, %)					
10	20	13	54	29	29	15
20	13	9	46	26	24	14
40	9	10	36	23	22	14
80	7	10	30	20	18	13

TABLE VIII—(*Continued*)

Cure (min. at 142° C)	A-8	B-8	C-8	D-8	E-8	F-8
	Stress at 300% elongation (lb./sq. inch)					
	Compression set (70 hr. at 70° C, %)					
10	25	10	57	40	36	20
	Compression set (70 hr. at 100° C, %)					
10	82	26	101	90	85	33
20	77	21	99	86	78	30
40	72	19	88	73	68	28
80	61	18	83	64	56	25
	Compression set (70 hr. at 121° C, %)					
40	85	27	93	80	81	38
	Heat build-up (° C)					
10	82	50	Soft	47	39	30
20	72	48	Soft	51	31	30
40	56	47	90	50	29	31
80	47	46	61	43	30	30

Type W compounds show lower moduli at lower elongations and higher moduli at the higher elongations than the comparable Neoprene Type GN compounds. In this respect, the stress-strain curves of the Neoprene Type W compounds approach those of natural rubber. Figure 5 illustrates these differences for

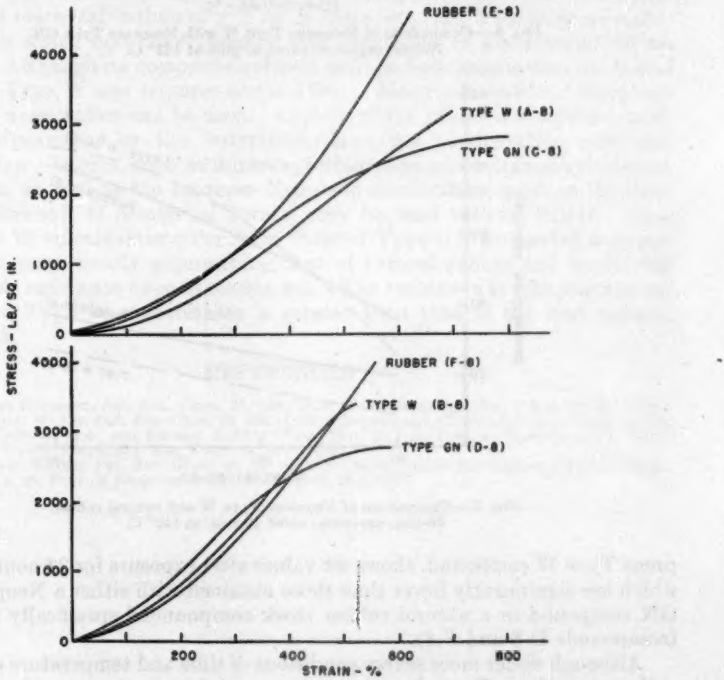


FIG. 5.—Comparison of stress-strain curves of natural rubber, Neoprene Type W, and Neoprene Type GN. Cured 20 min. at 153° C (307° F). *Above.* General purpose compounds. *Below.* Low compression set compounds.

compounds A-8, C-8, E-8 and B-8, D-8, F-8, respectively. The Neoprene Type W vulcanizates do not show the decrease in the ratio of stress to strain at high elongations which has hitherto been characteristic of chloroprene polymers.

The compression set data in Table VIII illustrate some of the most striking differences between vulcanizates of Neoprene Type E, and those of Neoprene Type GN or natural rubber. Compound A-8, for example, a conventional Neo-

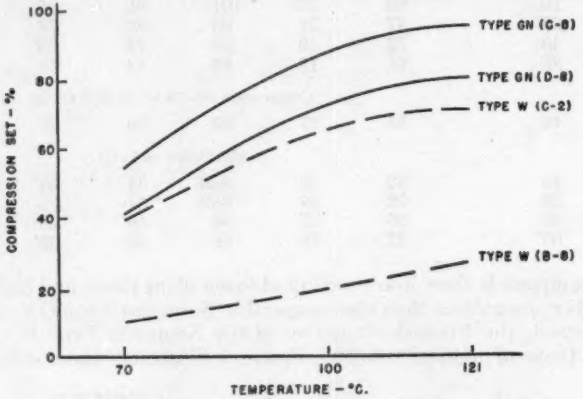


FIG. 6.—Comparison of Neoprene Type W with Neoprene Type GN. 70-hour exposure; cured 40 min. at 142° C.

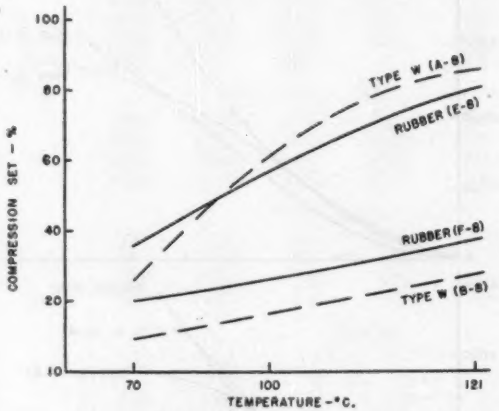


FIG. 7.—Comparison of Neoprene Type W and natural rubber. 70-hour exposure; cured 40 min. at 142° C.

prene Type W compound, shows set values after exposure for 22 hours at 70° C, which are significantly lower than those obtained with either a Neoprene Type GN compound or a natural rubber stock compounded specifically for low set (compounds D-8 and F-8).

Although under more severe conditions of time and temperature of exposure a Neoprene Type W stock such as compound A-8 continues to show excellent resistance to permanent deformation under compression, the advantage of a

nonsulfur cure such as that obtained with the di-*o*-tolylguanidine salt of dicatechol borate or 4,4′-diaminodiphenylmethane is evident. This is illustrated in Figures 6 and 7, in which the percentage compression set resulting from 70 hours' compression is plotted aginst the temperature of the exposure. In Figure 6 a comparison is made between Neoprene Types W and GN stocks in the presence and absence of the di-*o*-tolylguanidine salt of dicatechol borate. This figure includes a curve on compound C-2 from Table II, in addition to the compounds from Table VIII. The inherent low set of Neoprene Type W compounds is illustrated vividly by the unaccelerated Neoprene Type W stock containing only zinc oxide and magnesium oxide. The sets of this stock at various temperatures are less than those of an accelerated Neoprene Type GN stock.

It will be seen from Figure 7, that, over this temperature range, the conventional Neoprene Type W compound (A-8) cured with 2-mercaptothiazoline and sulfur is comparable in set properties to that of the conventional rubber compound (E-8), and that the Neoprene Type W compound accelerated with the di-*o*-tolylguanidine salt of dicatechol borate (B-8) is not only greatly superior to both of these stocks, but shows a decided advantage over a low set rubber stock (F-8) for the entire temperature range.

SUMMARY

Neoprene Type W, as a polymer, represents a fundamental departure from Neoprene Type GN in the manufacture of chloroprene polymers. This new Neoprene is more stable than any of its predecessors, and it contains no sulfur or chemicals which may decompose to give free sulfur or a vulcanization accelerator. Although its compounds should include both magnesium oxide and zinc oxide, Type W also requires acceleration. Many conventional Neoprene and rubber accelerators can be used. Certain of the rubber accelerators, such as diphenylguanidine or the butyraldehyde-aniline condensation products, require sulfur. Others, such as 2-mercaptothiazoline and tetramethylthiuram monosulfide, as well as the common Neoprene accelerators, such as the di-*o*-tolylguanidine salt of dicatechol borate, may be used without sulfur. Neoprene Type W vulcanizates differ from those of Type GN by having a stress-strain curve more nearly approaching that of natural rubber and by having much greater resistance to compression set. The resistance to compression set of Neoprene Type W vulcanizates is greater than that of the best natural rubber stock.

REFERENCES

[1] Bridgwater and Krismann, *Ind. Eng. Chem.* **25**, 280 (1933); Bridgwater, *Ind. Eng. Chem.* **26**, 33 (1934).
[2] Starkweather and Walker, *Ind. Eng. Chem.* **29**, 827 (1937); Torrence and Fraser, *Ind. Eng. Chem.* **31**, 939 (1939); Catton, Fraser, and Forman, Rubber Chem. Div., E. I. du Pont de Nemours & Co., Rept. 40–2, 15 (1940); Mayo, *Ind. Eng. Chem.* **42**, 696 (1950).
[3] Starkweather and Walker, *Ind. Eng. Chem.* **29**, 827 (1937); Catton, Fraser and Forman, Rubber Chem. Div., E. I. du Pont de Nemours & Co., Rept. 40–2, 15 (1940).

USE OF OXIDIZING AGENTS IN RUBBER VULCANIZATION

ZINC OXIDE-FREE PROCESS *

BERNARD C. BARTON

UNITED STATES RUBBER COMPANY, PASSAIC, N. J.

Before the advent of organic accelerators, many rubber compounds contained no zinc oxide. However, relatively large amounts of sulfur were required for desirable physical properties.

With the development of modern accelerators the use of zinc oxide, together with greatly reduced sulfur concentration, became the universal practice. When zinc oxide is not present in these low sulfur compounds, little or no vulcanization occurs.

Although the function of zinc oxide in the vulcanization reaction is not known with any degree of certainty, various suggestions as to the mechanism of its action have been made[1]. Consideration of these mechanisms has led to the elimination of zinc oxide and the replacement by certain mild oxidizing agents of a substantial proportion of the sulfur normally employed.

In the present paper the general development of the new process is described, oxidizing materials capable of eliminating zinc oxide are considered, and the mechanism of the vulcanization reaction is discussed.

SIMPLIFIED MECHANISM OF CONVENTIONAL VULCANIZATION

In spite of the complex nature of the reactions involved, a not too improbable overall mechanism of vulcanization can be proposed; it may be useful in directing investigations of the vulcanization process:

$$\underset{\text{Rubber hydrocarbon}}{RH} + S_x \xrightarrow{\text{Accelerator}} RSH + S_{x-1} \qquad (1)$$

$$2RSH + Zn^{++} \rightarrow RSZnSR + 2H^+ \qquad (2)$$

$$RSZnSR + S_x \rightarrow RSSR + ZnS + S_{x-1} \qquad (3)$$

Although hydrosulfide groups have not been determined experimentally in cured or semicured stocks, the vulcanization reaction is often assumed to involve the reaction of sulfur with the rubber hydrocarbon to form a rubber hydrosulfide as shown in Equation 1.

According to Hull, Olsen, and France[2] and Bloomfield[3] when zinc oxide is present in excess, as in rubber compounds, thiol groups form zinc mercaptides which are oxidized by sulfur in preference to the oxidation of the thiol itself. Therefore, it appears likely that when zinc oxide and fat acid are present, vulcanization proceeds through reactions involving the formation of a zinc mer-

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 42, No. 4, pages 671–674, April 1950. This paper was presented at the meeting of the Division of Rubber Chemistry of the American Chemical Society, Boston, Mass., May 23–25, 1949.

captide, as in Equation 2; this is oxidized by sulfur to give disulfide cross-links and zinc sulfide as shown in Equation 3.

Based on this simplified mechanism, vulcanization is a two-step oxidation process in which zinc oxide or zinc soap functions through its ability to form zinc mercaptides, which are more readily oxidized by sulfur to disulfide cross-links than are thiol groups.

If this mechanism is correct, oxidizing agents other than sulfur should be capable of taking the place of sulfur in the second step of the oxidation reaction. As zinc oxide or zinc soap is required only in the second step of the sulfur reaction, it is possible that the use of a suitable oxidizing agent would eliminate the necessity of these materials.

ELIMINATION OF ZINC OXIDE BY USE OF A SUITABLE OXIDIZING AGENT

In selecting an oxidizing agent for preliminary investigations, only those materials were considered which were strong enough to readily oxidize thiols but too weak to react rapidly with rubber. 2,2′-Dibenzothiazyl disulfide (MBTS) was selected for the initial examination. It readily oxidizes hydrogen sulfide to free sulfur and reacts relatively slowly with rubber.

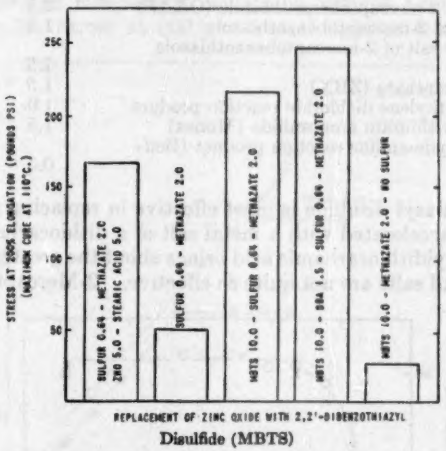

STRESS AT 200% ELONGATION (POUNDS PSI)
(MAXIMUM CURE AT 110°C.)
250
200
150
100
50
SULFUR 0.4% - METHAZATE 2.0
ZNO 5.0 - STEARIC ACID 5.0
SULFUR 0.4% - METHAZATE 2.0
MBTS 10.0 - SULFUR 0.4% - METHAZATE 2.0
MBTS 10.0 - ZNO 1.5 - SULFUR 0.4% - METHAZATE 2.0
MBTS 10.0 - METHAZATE 2.0 - NO SULFUR
REPLACEMENT OF ZINC OXIDE WITH 2,2'-DIBENZOTHIAZYL
Disulfide (MBTS)

FIG. 1.—Replacement of zinc oxide with 2,2′-dibenzothiazyl disulfide.

The effect of using MBTS in a zinc oxide-free Methazate-accelerated low sulfur compound is shown in Figure 1. To avoid reversion and other complicating side reactions which occur at higher more conventional curing temperatures, vulcanization was carried out at 110° C. The time of cure for each compound was selected to give the maximum physical cure.

The physical cure, as measured by stress at 200 per cent elongation, of a conventional low sulfur compound is shown in the first bar. Elimination of zinc oxide and stearic acid greatly reduces physical cure, as is shown in the second bar, and replacment of zinc oxide and stearic acid by MBTS increases physical cure, as shown in the third bar. The last bar shows that, in the absence of sulfur, MBTS is not a vulcanizing agent.

EFFECTIVENESS OF VARIOUS ACCELERATORS IN THE ZINC OXIDE-FREE PROCESS

A comparison of the effectiveness of various accelerators in the new process is shown in Table I.

TABLE I

EFFECT OF ACCELERATORS ON PHYSICAL CURE OF COMPOUNDS IN WHICH ZINC OXIDE IS REPLACED BY 2,2′-DIBENZOTHIAZYL DISULFIDE

Basic compound (parts per 100 grams of rubber): sulfur 0.64; dibenzylamine 1; 2,2′-dibenzothiazyl disulfide 8; all cures, 64 hours at 100° C (sufficient to combine all sulfur)

	Accelerator added (parts/100 g. rubber)	Stress at 200% elongation (lb./sq. inch)
None	..	100
Zinc salt of dimethyldithiocarbamic acid (Methazate)	1.5	225
Lead salt of dimethyldithiocarbamic acid (Ledate)	1.5	180
Copper (ic) salt of diethyldithiocarbamic acid (Cumate)	1.5	175
2-Mercaptobenzothiazole (MBT)	1.5	100
Zinc salt of 2-mercaptobenzothiazole (OXAF)	2.5	145
Silver salt of 2-mercaptobenzothiazole	1.5	115
Copper (ic) salt of 2-mercaptobenzothiazole (Cuprax)	1.5	115
Zinc butylxanthate (ZBX)	1.5	115
Ammonia-ethylene dichloride reaction product	1.0	100
Tetramethylthiuram monosulfide (Monex)	1.5	100
Butyraldehyde-aniline reaction product (Beutene)	0.5	90

2,2′-Dibenzothiazyl disulfide is most effective in replacing zinc oxide when the compound is accelerated with a metal salt of a dithiocarbamic acid. The zinc salt of dimethyldithiocarbamic acid brings about the greatest physical cure; the copper and lead salts are not quite so effective. 2-Mercaptobenzothiazole,

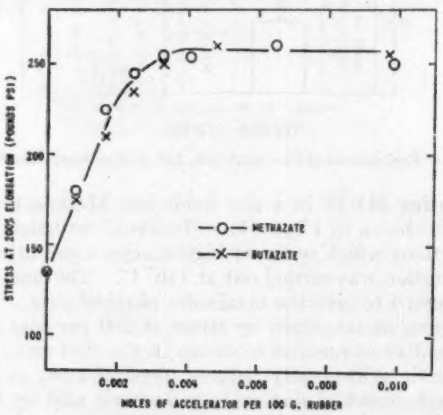


FIG. 2.—Effect of accelerator content on physical cure. Compounds contained sulfur, 0.64 part; MBTS, 10 parts; dibenzylamine, 1.5 parts; and variable amounts of Methazate and Butazate per 100 grams of rubber; all cures, 32 hours at 100° C.

the zinc, silver, and copper salts of 2-mercaptobenzothiazole, zinc butylxanthate, an ammonia-ethylene dichloride reaction product, tetramethylthiuram disulfide, and a butyraldehyde-aniline reaction product were of no appreciable value.

EFFECT OF ACCELERATOR CONTENT ON PHYSICAL CURE

The effects of increasing amounts of Methazate and Butazate (the zinc salts of dimethyl- and dibutyldithiocarbamic acid) on the physical cure of a compound containing 0.64 part of sulfur and 10 parts of MBTS are shown in Figure 2. All compounds were cured for a sufficient time to combine all sulfur.

The physical cure increases with increasing accelerator content up to a definite point, above which further additions have no effect. At equivalent molecular concentrations, Methazate and Butazate are equally effective. About 0.0035 mole is required to give maximum physical cure in a compound containing 0.02 gram atoms of sulfur (0.64 part) and 10 parts of MBTS.

EFFECT OF CONCENTRATION OF 2,2'-DIBENZOTHIAZYL DISULFIDE ON PHYSICAL CURE

The effect of concentration of MBTS on the extent of vulcanization of Methazate-accelerated compounds containing various amounts of sulfur is shown in Figure 3. Stress at 200 per cent elongation increases in a linear

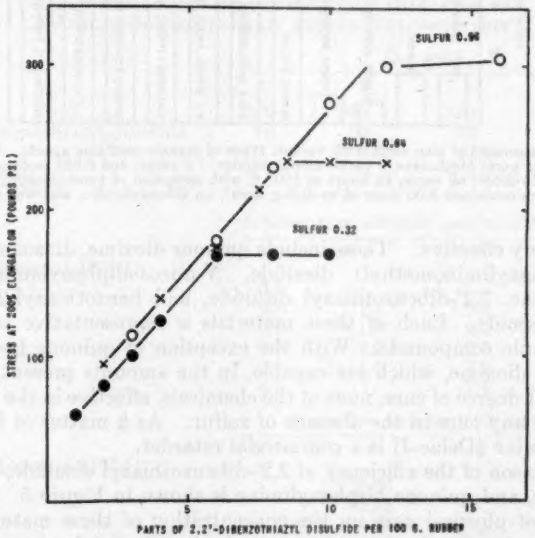


FIG. 3.—Effect of 2,2'-dibenzothiazyl disulfide content on physical cure. Compounds contained sulfur as shown; Methazate, 2 parts; dibenzylamine, 1 part; and variable amounts of MBTS per 100 grams of rubber; all cures, 32 hours at 100° C.

manner with increasing MBTS concentration up to a maximum for each amount of sulfur, beyond which further additions have little or no effect. When there is a deficiency of MBTS, the degree of vulcanization is independent of sulfur concentration and directly dependent on the concentration of MBTS. On the

other hand, when sufficient oxidizing agent is present to give a maximum degree of vulcanization for a given amount of sulfur, the extent of vulcanization is dependent on the amount of sulfur present.

EFFECTIVENESS OF VARIOUS OXIDIZING AGENTS IN NEW PROCESS

In Figure 4 replacement of zinc oxide and fatty acid with various types of organic oxidizing agents is shown. Although the materials are not completely representative of all types of organic oxidizing agents, some conclusions can be obtained. The stronger oxidizing agents, such as quinone, benzoyl peroxide, and cumene hydroperoxide, are ineffective, whereas various milder oxidizing

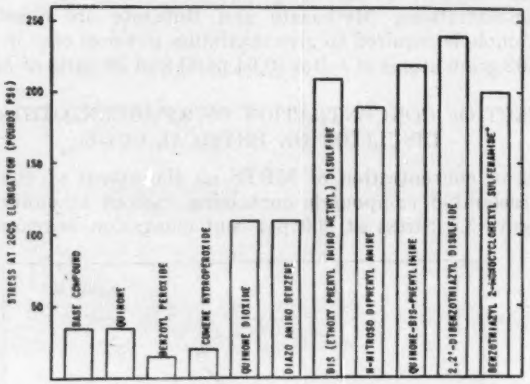


FIG. 4.—Replacement of zinc oxide with various types of organic oxidizing agents. Compounds contained sulfur, 0.64 part; Methazate, 2 parts; dibenzylamine, 1.5 parts; and 0.025 mole of oxidizing agent per 100 grams of rubber; all cures, 32 hours at 100° C with exception of benzothiazyl-2-monocyclohexyl sulfonamide which contained 0.05 mole of oxidizing agent, no dibenzylamine, and was cured 8 hours at 212° F.

agents are very effective. These include quinone dioxime, diazoaminobenzene, bis(ethoxyphenyliminomethyl) disulfide, *N*-nitrosodiphenylamine, quinone bisphenylimine, 2,2′-dibenzothiazyl disulfide, and benzothiazyl-2-monocyclohexyl sulfenamide. Each of these materials is representative of a different class of organic compounds. With the exception of quinone bisphenylimine and quinone dioxime, which are capable, in the amounts present, of bringing about a slight degree of cure, none of the chemicals, effective in the new process, brings about any cure in the absence of sulfur. As a matter of fact *N*-nitrosodiphenylamine (Delac-J) is a commercial retarder.

A comparison of the efficiency of 2,2′-dibenzothiazyl disulfide, *N*-nitrosodiphenylamine, and quinone bisphenylimine is shown in Figure 5. The similar dependence of physical cure on the concentration of these materials of such widely different molecular structure suggests that the mechanism of vulcanization with these materials is essentially the same.

REDUCTION OF 2,2′-DIBENZOTHIAZYL DISULFIDE TO 2-MERCAPTOBENZOTHIAZOLE DURING VULCANIZATION

2,2′-Dibenzothiazyl disulfide (MBTS) oxidizes low-molecular weight thiols to disulfides, as shown in Equation 4. However, because of the reducing char-

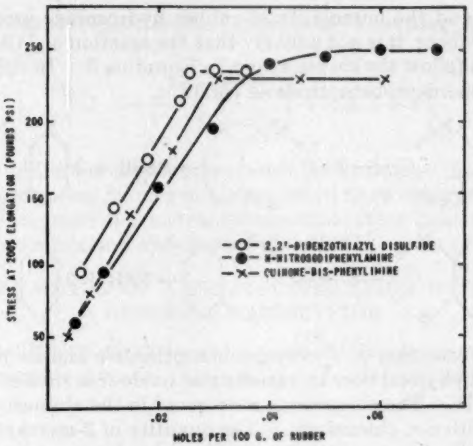


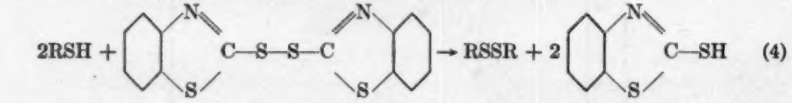
FIG. 5.—Effect of equivalent amounts of three effective oxidizing agents on physical cure. Compounds contained sulfur, 0.64, and Methazate, 2 parts; maximum physical cure at 100° C.

TABLE II

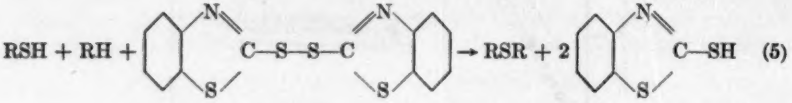
REDUCTION OF 2,2'-DIBENZOTHIAZOLE DISULFIDE TO 2-MERCAPTOBENZOTHIAZOLE DURING VULCANIZATION

	Compound			
	A	B	C	D
Rubber	100	100	100	100
2,2'-Dibenzothiazyl disulfide	10	10	10	10
Sulfur	..	0.64	0.64	0.64
Methazate	..	..	2.00	2.00
Dibenzylamine	..	..	..	1.50
	2-Mercaptobenzothiazole, parts per 100 g. rubber			
	A	B	C	D
Cured, hours at 100° C				
0	0.5	..	..	..
2	0.8	1.1	5.4	6.6
4	0.9	1.9	6.1	6.7
8	1.3	2.2	6.5	7.2
16	2.9	4.4	7.1	7.3
32	4.0	..	7.1	7.3
	Free sulfur, parts per 100 g. rubber			
	A	B	C	D
Cured, hours at 110° C				
2	..	0.58	..	0.05
4	..	0.45	..	0.06
8	..	0.35	..	0.05
16	..	0.24	0.05	0.05
	Stress at 200% elongation (lb./sq. in.)			
	A	B	C	D
Cured, hours at 110° C				
2	15	20	165	225
4	25	30	180	245
8	15	60	205	245
16	20	60	215	225
32	25	45	200	210

acter of rubber and the immobility of rubber hydrosulfide groups in cured or partially cured rubber, it is not unlikely that the reaction of MBTS with rubber hydrosulfide can follow the course shown in Equation 5. In either case MBTS is reduced to 2-mercaptobenzothiazole (MBT):



(4)



(5)

The rate of formation of 2-mercaptobenzothiazole and its relation to combined sulfur and physical cure in various zinc oxide-free rubber compounds are shown in Table II. The compounds were cured in the absence of air at 110° C and extracted with C.P. chloroform. The quantity of 2-mercaptobenzothiazole present in the chloroform extract was determined by measuring the optical density of the choloroform solution at 3260 A. with a Beckman spectrophotometer.

The data in Table II clearly show that the formation of 2-mercaptobenzothiazole in compounds B, C, and D is associated with the combination of sulfur with rubber and with the development of physical cure. The combination of sulfur in compound B, even though at a slow rate, results in faster formation of 2-mercaptobenzothiazole than occurs in compound A, in which no sulfur is present. In compounds C and D, in which rapid combination of sulfur occurs, a corresponding increase in rate of formation of 2-mercaptobenzothiazole is found. This formation is related to the rapid development of physical cure.

In compounds C and D, combination of all the sulfur (0.02 gram atom) was accompanied by the formation of 6.6 to 6.8 parts (0.040 to 0.041 mole) of 2-mercaptobenzothiazole. This corresponds to the complete reduction of 1 mole of 2,2′-dibenzothiazyl disulfide for each gram atom of sulfur combined with the rubber and suggests that the oxidation of the rubber hydrosulfide occurs according to Equation 5.

The progress of the reaction of the disulfide with rubber alone (formulation A, Table II) was followed by determining both MBTS and 2-mercaptobenzothiazole in the chloroform extract. The amount of MBTS was obtained from the optical density of the chloroform solution at 2750 A. These results are shown in Table III.

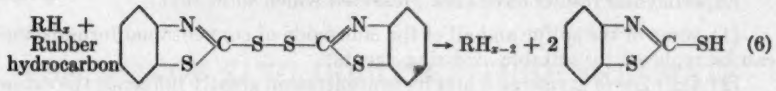
TABLE III

REACTION OF 2,2′-DIBENZOTHIAZYL DISULFIDE WITH RUBBER ALONE

	Cure, hours at 110° C					
	0	2	4	8	15	32
	Parts per 100 grams rubber					
2,2′-Dibenzothiazyl disulfide	9.3	9.0	8.9	8.4	6.6	5.2
2-Mercaptobenzothiazole	0.5	0.8	0.9	1.3	2.9	4.0

The data given in Table III show that 2,2′-dibenzothiazyl disulfide reacts relatively slowly with rubber at 110° C, the reaction being only about 45 per cent completed in 32 hours. The results also show that little combination of 2-mercaptobenzothiazole with rubber occurs during this reaction. About 85 per cent of the disulfide which reacts with rubber in 32 hours at 110° C is con-

verted to 2-mercaptobenzothiazole, apparently according to the following reaction:



(6)

In this reaction additional unsaturation must be introduced into the rubber hydrocarbon. Farmer and Shipley in (Bloomfield[4]) have observed the formation of considerable amounts of 2-mercaptobenzothiazole on heating together 2,2'-dibenzothiazyl disulfide and cyclohexene at 140° C.

REACTION OF A THIAZYL DISULFIDE WITH RUBBER HYDROSULFIDE

Evidence that thiazyl disulfides are capable of vulcanizing rubber containing hydrosulfide groups is given in Figure 6. In the investigation described here,

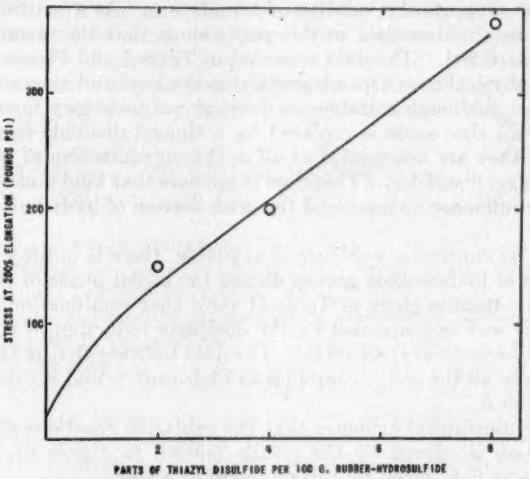


FIG. 6.—Vulcanization of rubber hydrosulfide with thiazyl disulfide. Cure, 16 hours at 100° C; stress at 200% elongation was calculated from swelling index of vulcanizates in xylene.

rubber hydrosulfide was vulcanized by the use of Erie accelerator, a benzene-soluble mixture of 4,5-dimethyl- and 4-ethylthiazyl disulfide. No other compounding ingredients were employed.

The rubber hydrosulfide containing about 2 parts of thiol sulfur per 100 grams of rubber was prepared by light-initiated addition of hydrogen sulfide to rubber in a 2 per cent benzene solution. Various amounts of the disulfide were added to this solution, and films were prepared by evaporating the solutions in a stream of purified nitrogen. The dried films were sealed in evacuated tubes and cured 16 hours at 100° C. Stress at 200 per cent elongation was estimated from the degree of swelling of the cured films in xylene.

In the absence of thiazyl disulfide, no vulcanization occurs in the rubber-hydrosulfide films. When the disulfide is present, the stress at 200 per cent elongation is roughly a linear function of its concentration. These experiments offer conclusive evidence that rubber hydrosulfide can be cured by thiazyl disulfides alone.

SUMMARY OF EXPERIMENTAL RESULTS

Experimental results have been presented which show that:

(1) some of the sulfur and all of the zinc oxide of conventional formulations can be replaced by suitable oxidizing agents;

(2) the type of accelerator and its concentration greatly influence the extent of physical cure;

(3) in vulcanization with 2,2′-dibenzothiazyl disulfide, the formation of 2-mercaptobenzothiazole is associated with the combination of sulfur and with the development of physical cure;

(4) Rubber containing hydrosulfide groups can be vulcanized by thiazyl disulfides alone.

POSTULATED MECHANISM OF VULCANIZATION

The experimental results presented support the mechanism of vulcanization shown in Equations 1 and 5. No experimental evidence has been presented which directly supports the validity of Equation 1. As a matter of fact, the experimental results described in this paper show that the reaction has been greatly oversimplified. The data recorded in Table I and Figure 2 show that the extent of physical cure depends greatly on the kind and amount of accelerator employed. Although suitable accelerators are necessary for efficient vulcanization when zinc oxide is replaced by a thiazyl disulfide in conventional formulations, they are not needed at all in the vulcanization of rubber hydrosulfide by thiazyl disulfides. Therefore it appears that kind and concentration of accelerator influence amount and (or) distribution of hydrosulfide formed in Equation 1.

Although no conclusive evidence is available, there is indirect evidence for the formation of hydrosulfide groups during the initial phase of the vulcanization reaction. Results given in Table II show that combination of 0.02 gram atom of sulfur was accompanied by the complete reduction of 0.021 to 0.022 mole of 2,2′-dibenzothiazyl disulfide. The data indicate that in these formulations practically all the sulfur combines as hydrosulfide and is oxidized according to Equation 5.

Strong circumstantial evidence that the oxidation reactions described lead to vulcanization is offered by the results (shown in Figure 6) when rubber hydrosulfide was vulcanized by thiazyl disulfide alone.

SUMMARY

Conventional vulcanization may be considered as a two-step oxidation process in which zinc oxide functions through its ability to form zinc mercaptides by reacting with rubber hydrosulfides formed in the first step. These zinc mercaptides are then oxidized by sulfur to disulfide cross-links. Consideration of this mechanism has led to the development of a new vulcanization process in which various mild organic oxidizing agents replace sulfur in the second step of the oxidation process and thereby make possible the elimination of zinc oxide. Oxidizing materials capable of replacing a portion of the sulfur normally used are considered, and the mechanism of the new vulcanization reaction is discussed.

REFERENCES

[1] Armstrong, Little, and Doak, *Ind. Eng. Chem.* **36**, 628 (1944); Hull, Olsen, and France, *Ind. Eng. Chem.* **38**, 1282 (1946).
[2] Hull, Olsen, and France, *Ind. Eng. Chem.* **38**, 1282 (1946).
[3] Bloomfield, *J. Soc. Chem. Ind.* **67**, 16 (1948).
[4] Bloomfield, *J. Chem. Soc.* **1947**, p. 1549.

THE USE OF ZINC DIBUTYLDITHIOCARBAMATE IN THE MANUFACTURE OF CELLULAR RUBBER *

ADRIEN HAEHL

INSTITUT FRANÇAIS DU CAOUTCHOUC, PARIS, FRANCE

The manufacture of cellular rubber has made considerable progress in recent years, and today it is uncommon to find a rubber company which does not make this sort of product. But in spite of the appearance of organic blowing agents, most sponge rubber is still manufactured with the aid of conventional swelling agents, *i.e.*, ammonium carbonate, sometimes ammonium bicarbonate, and finally, mixtures of sodium bicarbonate and a fatty acid. Of these three blowing agents, mixtures of sodium bicarbonate and a fatty acid are the most common because such a combination is much simpler to handle than are ammonium salts.

SWELLING AGENTS

AMMONIUM CARBONATE

Ammonium carbonate commences to decompose at 58° C, and its decomposition is complete at 120° C. Ammonium bicarbonate, used much less widely, decomposes between 36° and 60° C.

The low temperature of decomposition of ammonium carbonate may lead to certain difficulties in the manufacture of cellular rubber. First of all, if the rubber mixture becomes too hot during incorporation of the carbonate, there is a loss of gas, and, as a result, an insufficient quantity is then available for adequate blowing in the mold. Since, as has been pointed out, ammonium carbonate begins to decompose at the very low temperature of 58° C, it is necessary to put the rubber mixture in a cold mold, and it is necessary also that the rise in temperature during the period of blowing be constant in successive operations. However, it is very difficult to control successfully the rise in a temperature range below 100° C; consequently, there is a tendency for the blowing to vary, and it has been found that the pores in cellular rubber made with ammonium salts are always more irregular in number, form, and size than those obtained when a mixture of sodium bicarbonate and a fatty acid is employed.

It might be pointed out that a method for stabilizing ammonium carbonate in rubber mixtures has been described. According to a patent of Hardmann[1], there is less tendency to blow at low temperatures if the ammonium carbonate is transformed into a complex zinc derivative. To accomplish this, a high proportion of zinc oxide is added to the rubber mixture, and, after incorporation of the ammonium carbonate, the mixture is finally passed several times through cold mill rolls to bring about the reaction. Whether or not this method is in use at present is uncertain.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 27, No. 4, pages 205–208, April 1950. This paper was presented before the Association Française des Ingenieurs du Caoutchouc, December 15, 1949.

MIXTURES OF SODIUM BICARBONATE AND A FATTY ACID

In view of the difficulties involved in the use of ammonium salts, mixtures of sodium bicarbonate and a fatty acid are in current use today.

Sodium bicarbonate itself commences to decompose at 120° C, a temperature at which decomposition of ammonium carbonate is already complete, but it does not decompose to any considerable extent until a temperature of 150° C is reached. Addition of a fatty acid to a rubber mixture containing sodium bicarbonate does not change the temperature at which decomposition begins, for this remains at 120° C, but its addition does bring about a much more intense evolution of gas at temperatures above 120° C, so that even at 130° C there is a considerable evolution of gas, and this becomes stronger at 140° C. However, even under these conditions, to obtain cellular rubber of low density, the temperature must be at least 150° C.

It should be mentioned at this point that sodium bicarbonate, and likewise ammonium carbonate and bicarbonate, have the serious fault of not being compatible with rubber. They do not disperse well at all in rubber mixtures, even if the latter have been prepared with all reasonable precautions.

Because of this poor dispersion of sodium bicarbonate, the practical technologist has been obliged to raise the proportion of the sodium bicarbonate to the fatty acid. If the ratio of sodium bicarbonate to stearic acid theoretically required to form carbon dioxide, water, and sodium stearate is calculated, it will be found that almost 0.3 part of sodium bicarbonate per 1 part of stearic acid is required, whereas in practice 1 to 2 parts of sodium bicarbonate per 1 part of stearic acid is used. There is, therefore, in the rubber mixture an excess of sodium bicarbonate which remains as a filler.

On the other hand, tests by the present author show that if sodium bicarbonate is incorporated into the rubber in the form of a dispersion in oil, *i.e.*, in a form which is compatible with the rubber, perfect blowing is obtained when the two agents are used in the theoretical proportion of 1 part of sodium bicarbonate to 3.4 parts of stearic acid.

ADAPTATION OF VULCANIZING AGENTS TO THE SWELLING AGENTS

It has been pointed out that rubber can be made to blow in the range of 120° to 150° C by a mixture of sodium bicarbonate and a fatty acid. This range includes the ordinary temperatures of vulcanization, and it is necessary not only to adapt the vulcanizing agents to the blowing agent but vice versa. In the cellular rubber, the sodium bicarbonate-stearic acid-sulfur-accelerator mixture comprises a system each element of which can be regarded as a function of each of the others. It might even be said that the structure of cellular rubber depends to a greater extent on the accelerator than it does on the blowing agent.

As a matter of fact, if the acceleration is too rapid, the mixture begins to vulcanize before blowing is complete, and the cellular rubber does not fill the mold completely or take the form desired. If, on the contrary, the acceleration is too slow, the cellular rubber remains soft and flabby after blowing is complete. The carbon dioxide, which is very soluble in rubber, in this case diffuses to the outside, the gas pressure within the cells decreases, and the cellular rubber collapses.

Satisfactory acceleration of a cellular rubber mixture is, therefore, one which allows blowing to continue to the point where the mold is completely filled and,

at the same time, starts the vulcanization process immediately after blowing is complete.

It has been found that a mixture of zinc dibutyldithiocarbamate and benzothiazolyl disulfide is a particularly suitable combination for the manufacture of cellular rubber.

The idea of reducing the quick action of zinc dialkyldithiocarbamates by benzothiazolyl disulfide is not new. This problem has already been studied and information on the subject has already been published[2]. This work was concerned with zinc dimethyldithiocarbamate, zinc diethyldithiocarbamate, and zinc dibutyldithiocarbamate, with particular attention to the dimethyl and diethyl derivatives. Unfortunately curves showing the time when vulcanization begins, which would be very useful in the formulation of mixtures for cellular rubber, were not given in this work. It, therefore, seemed advisable to study this problem further, with particular attention to the butyl derivative. Zinc dibutyldithiocarbamate is, in fact, by far the most soluble in rubber, and this solubility guarantees perfect dispersion in the rubber mixture, a dispersion which is essential to the rapid onset of vulcanization as soon as blowing is complete.

USE OF ZINC DIBUTYLDITHIOCARBAMATE ALONE OR WITH AN EQUAL QUANTITY OF BENZOTHIAZOLYL DISULFIDE

Zinc dibutyldithiocarbamate alone is a very quick acting ultra-accelerator, and therefore is used in self-curing cements. This accelerator has also found numerous applications in the latex industry, where its tendency to cause rapid vulcanization can have no effect. However, it is inadvisable to use it alone in dry mixtures.

TABLE I

ZINC DIBUTYLDITHIOCARBAMATE ALONE AS ACCELERATOR AND AS AN ACCELERATOR IN THE PRESENCE OF BENZOTHIAZOLYL DISULFIDE

Ingredients	Mixture 1	Mixture 2
Smoked sheet rubber	100	100
Sulfur	1	1
Zinc dibutyldithiocarbamate	0.5	0.5
Benzothiazolyl disulfide	—	0.5
Stearic acid	1	1
Zinc oxide	5	5
	107.5	108.

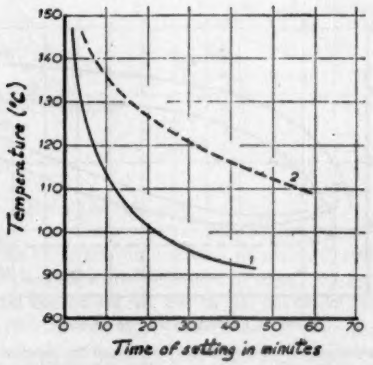


FIG. 1.—Curves showing the times of setting at different temperatures of Mixtures 1 and 2.

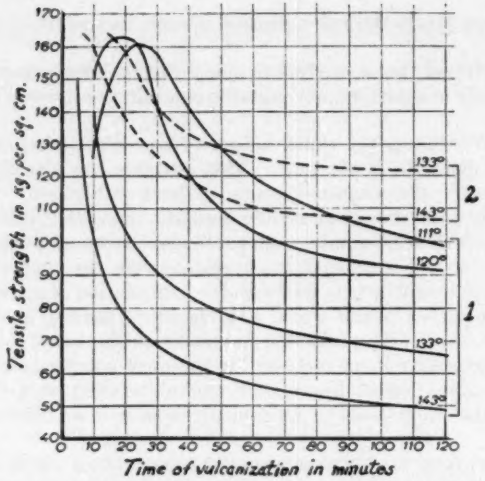


FIG. 2.—Curves showing tensile strength as a function of the time of vulcanization of Mixture 1 (zinc dibutyldithiocarbamate alone) and of Mixture 2 (zinc dibutyldithiocarbamate and benzothiazolyl disulfide in combination).

An examination of the scorching curve showing the times at which the rubber mixture accelerated by zinc dibutyldithiocarbamate alone begins to vulcanize (see Figure 1) shows that this curve has a very sharp descent, which is an indication of difficulties likely to be encountered in mixing, calendering, and extrusion, even in the case of a mixture like the one shown, which contains only 1 per cent of sulfur based on the rubber.

On the other hand, an examination of the vulcanization curves of the rubber mixture accelerated with zinc dibutyldithiocarbamate alone (see Figure 2) shows this mixture to be of no practical interest. The tensile strength curves are, in fact, very steep, and none shows any plateau for temperatures of 133° and 143° C. The corresponding elongation curves (see Figure 3) show very early reversion.

The tensile strength curves of the same mixture for temperatures of 111° and 120° C show optimum points at which the times of vulcanization correspond to

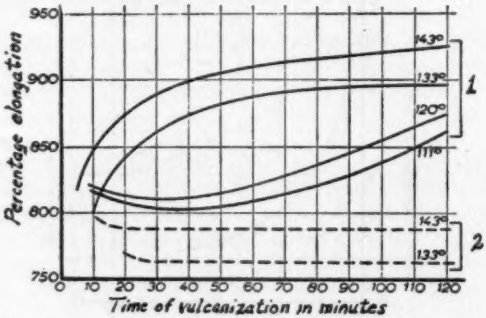


FIG. 3.—Curves showing elongation at rupture as a function of the time of vulcanization of Mixture 1 (zinc dibutyldithiocarbamate alone) and a Mixture 2 (zinc dibutyldithiocarbamate and benzothiazolyl disulfide in combination).

those of rubber mixtures accelerated by thiuram compounds, which are also much less quick-acting and give much flatter vulcanization curves at these temperatures.

It is not, therefore, advisable to use zinc dibutyldithiocarbamate alone as an accelerator.

Far different results are obtained, however, if 0.5 part of benzothiazolyl disulfide is added as an accessory agent. The curve of scorching (Figure 1, curve 2) becomes much less steep; in other words, the rubber mixture has much less tendency to begin to vulcanize prematurely. At 110° C, then, the time for the mixture to begin to vulcanize is 60 minutes instead of 11 minutes with the ultra-accelerator alone. In general, the time to begin to vulcanize is reduced to about $\frac{1}{3}$, $\frac{1}{4}$, $\frac{1}{5}$, and $\frac{1}{7}$ of its original value for temperatures of 110°, 120°, 130°, and 140° C, respectively; finally the curves join in the region of 150° C.

The addition of benzothiazolyl disulfide to a rubber mixture accelerated primarily with zinc dithiocarbamate also changes to a considerable extent the vulcanization curves at 133° and 143° C. The tensile strength curves (the broken-line curves in Figure 2) are much less steep after the points of optimum vulcanization have been passed. The elongation curves (broken-line curves in Figure 3) are practically straight lines, without any sign of reversion. Any danger of overcuring is, therefore, very small, and this is a very important feature in cellular rubber mixtures, which are sometimes vulcanized in very thick units.

USE OF VARIOUS PROPORTIONS OF ZINC DIBUTYLDITHIOCARBAMATE AND BENZOTHIAZOLYL DISULFIDE AS ACCELERATORS AND OF SULFUR

If the proportion of zinc dibutyldithiocarbamate is reduced in favor of benzothiazolyl disulfide, it is necessary to increase the percentage of sulfur. By doing this, mixtures are obtained, as shown in Table 2, where the benzothiazolyl disulfide becomes the primary accelerator and zinc dibutyldithiocarbamate is its activator. The percentages of sulfur remain relatively low, for they must still conform to the percentages required for the benzothiazolyl disulfide in conjunction with the zinc dibutyldithiocarbamate.

TABLE 2

CHANGES IN ACCELERATORS AND IN SULFUR

Ingredients	Mixture 3	Mixture 4	Mixture 5*
Smoked sheet rubber	100	100	100
Sulfur	2	1.5	1
Benzothiazolyl disulfide	0.9	0.8	0.5
Zinc dibutyldithiocarbamate	0.1	0.2	0.5
Stearic acid	1	1	1
Zinc oxide	5	5	5
	109	108.5	108

* Mixture 5 is identical to Mixture 2 in Table 1.

A comparison of the time for the control mixture (Mixture 5 containing 0.5 part of benzothiazolyl disulfide and 0.5 part of zinc dibutyldithiocarbamate) to begin to vulcanize with the times for the mixtures containing a preponderance of benzothiazolyl disulfide shows that a decrease in the amount of zinc dibutyldithiocarbamate in favor of an increase in the amount of benzothiazolyl disulfide improves only insignificantly the vulcanization curve (see Figure 4). In

this case, as was confirmed by further experiments in mixtures accelerated by a combination of benzothiazolyl disulfide and zinc dibutyldithiocarbamate, the increase in proportion of sulfur has a greater influence on the vulcanization curves than does the increase in proportion of benzothiazolyl disulfide and accompanying decrease in proportion of zinc dibutyldithiocarbamate.

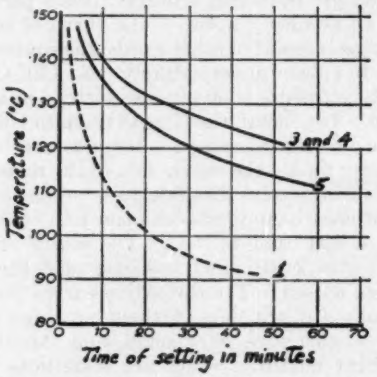


FIG. 4.—Curves showing time of setting as a function of the temperature of Mixtures 3, 4, and 5 containing different proportions of benzothiazolyl disulfide and zinc dibutyldithiocarbamate and of sulfur. The broken curve represents a mixture containing zinc dibutyldithiocarbamate alone.

An examination of the tensile strength curves in Figure 5 shows higher values for mixtures containing relatively high proportions of sulfur, as was to be expected; nevertheless, the trends of the curves are the same in the three cases. The experimental values for the elongations are practically the same in the three cases.

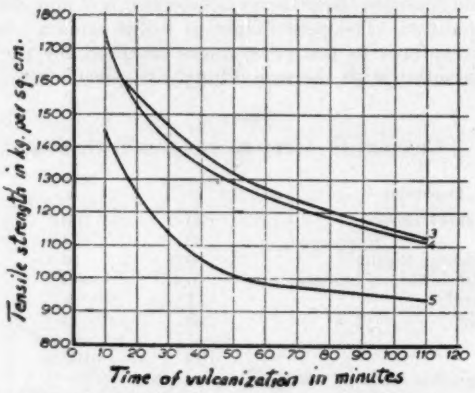


FIG. 5.—Curves showing tensile strength as a function of the time of vulcanization (3 kg. per sq. cm. steam pressure) of Mixtures 3, 4, and 5.

In the case of a rubber mixture designed for a cellular product, the rapidity of heating to an elevated temperature plays a more important part than does the toughness of the mixture. It is of advantage, then, from the viewpoint of equal or nearly equal safety, to choose the mixture which vulcanizes most rapidly, *i.e.*, to choose a ratio of accelerators close to 1.

CHANGES IN THE PROPORTION OF ACCELERATORS IN THE PRESENCE OF A FIXED PROPORTION OF 2.5 PER CENT OF SULFUR

In a third series of experiments, a base mixture containing 2.5 per cent of sulfur and benzothiazolyl disulfide as accelerator was used as the starting point. In this mixture, the benzothiazolyl disulfide was replaced progressively by zinc dibutyldithiocarbamate, as shown in Table 3.

TABLE 3

CHANGES IN THE PROPORTION OF ACCELERATORS IN THE PRESENCE OF 2.5 PER CENT OF SULFUR

Ingredients	Mixture 6	7	8	9
Smoked sheet rubber	100	100	100	100
Sulfur	2.5	2.5	2.5	2.5
Benzothiazolyl disulfide	0.7	0.6	0.5	0.35
Zinc dibutyldithiocarbamate	—	0.1	0.2	0.35
Stearic acid	1	1	1	1
Zinc oxide	5	5	5	5
	109.2	109.2	109.2	109.2

It was found in this series of tests that, as a result of the higher percentage of sulfur, the curves of setting (see Figure 6) become progressively steeper as the proportion of zinc dibutyldithiocarbamate increases. Nevertheless, the four rubber mixtures in the series were stored for five months at room temperature without showing any indication whatever of scorching.

The tensile strength curves (see Figure 7) show that the time of vulcanization is shortened considerably by the replacement of benzothiazolyl disulfide by zinc dibutyldithiocarbamate in the base mixture. At the same time the absolute values of the tensile strength increase greatly, an indication of the activating effect of zinc dibutyldithiocarbamate. This increase in tensile strength is accompanied by a very small loss in extensibility, but this is not of great significance.

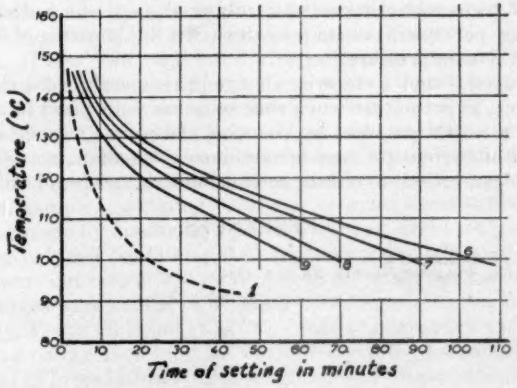


FIG. 6.—Curves showing time of setting as a function of the temperature of Mixtures 6, 7, 8, and 9, containing a fixed content of 2.5 per cent of sulfur but different proportions of benzothiazolyl disulfide and zinc dibutyldithiocarbamate. The broken curve represents a mixture containing zinc dibutyldithiocarbamate alone and 1 per cent sulfur.

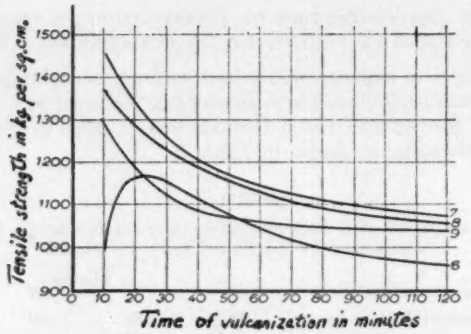


FIG. 7.—Curves showing tensile strength as a function of the time of vulcanization (3 kg. per sq. cm. steam pressure) of Mixtures 6, 7, 8, and 9.

CONCLUSIONS

One conclusion to be drawn from the present work is that a combination of zinc dibutyldithiocarbamate and benzothiazolyl disulfide is a particularly advantageous one for the manufacture of cellular rubber. By means of this combination of accelerators it is possible, by proper balancing of their proportions and of the percentage of sulfur, to adjust at will the stability of the rubber mixture with respect to blowing and to the rate of vulcanization as soon as blowing is complete. The good solubility of zinc dibutyldithiocarbamate in rubber guarantees a very rapid onset of vulcanization after the blowing action.

It is evident that the most suitable method for manufacturing cellular rubber products is stepwise vulcanization. At the beginning, for example, heating may be at a temperature corresponding to 2 kg. per sq. cm. steam pressure, which allows satisfactory blowing of the rubber mixture; following this the temperature is raised rapidly to a point corresponding to 4 kg. per sq. cm. steam pressure as soon as the blowing effect is complete. At this higher temperature, vulcanization of the cellular rubber becomes very rapid. By this method it was found possible to manufacture cellular rubber shoes by an initial heating of 5 minutes at 2 kg. per sq. cm. steam pressure and a final heating of 5 minutes at 4 kg. per sq. cm. steam pressure.

However, even if such a stepwise change in temperature during the heating is impracticable, as is the case when shoe soles are vulcanized in an electrically heated press, it is still possible, by choosing the proper proportions of sulfur, zinc dibutyldithiocarbamate, and benzothiazolyl disulfide, as well as the temperature of vulcanization, to obtain perfect blowing and rapid vulcanization.

REFERENCES

[1] Hardmann, U. S. patent 2,200,473.
[2] R. T. Vanderbilt Co., *Vanderbilt News* 11, No. 5, 4 (1941).

STABILITY OF CRUDE GR-S

EFFECT OF TRACES OF ANTIOXIDANT *

E. J. GLAZER, C. R. PARKS, J. O. COLE, AND J. D. D'IANNI

THE GOODYEAR TIRE & RUBBER COMPANY, AKRON, OHIO

It has been observed in this laboratory that different batches of crude GR-S, containing no deliberately added antioxidant, varied widely in stability. In some cases evidence of oxidation was noted, either at the end of the drying period, or on aging for several weeks at room temperature. In other cases the stability of the polymer appeared to be comparable to standard GR-S which contained antioxidant.

In an attempt to explain these observations it was postulated that traces of antioxidant, picked up from processing equipment, had an appreciable effect on the stability of the polymer. The object of the present work was to obtain information on the stability of antioxidant-free GR-S and to determine whether traces of antioxidant had any significant effect on the stability of crude GR-S toward oxygen.

EXPERIMENTAL

Polymer samples were prepared by the mutual formula[1] at 45° C to a conversion of 70 per cent. Glass or stainless steel equipment was employed to minimize contamination. The degassed latex was shortstopped with 0.1 part of sodium sulfide, antifoam A was added, and the styrene completely stripped by steam distillation at reduced pressure. The temperature of the latex did not exceed 50° C during the distillation. The required amount of phenyl-β-naphthylamine (PBNA) was added as a 0.3 per cent and a 3 per cent dispersion, respectively, to give an antioxidant content of 0.01 and 0.1 per cent. The dispersions were made by blending a 10 per cent benzene solution of phenyl-β-naphthylamine with a 0.5 per cent solution of Nacconol-NRSF in a hand homogenizer. Latex was coagulated with salt-acetic acid, and the coagulated polymer was washed thoroughly with warm water on a wash mill. One series of samples was immediately vacuum dried for 20 hours at 60° C under 15 mm. of pressure in an all-glass system frequently flushed out with oxygen-free nitrogen. Another series was dried in a circulating air oven for 11 hours at 88° C. The antioxidant-free controls were dried separately to avoid any contamination. An additional sample containing 0.001 per cent phenyl-β-naphthylamine was prepared in benzene by dissolving 9 parts of vacuum dried control and 1 part of vacuum dried polymer containing 0.01 per cent phenyl-β-naphthylamine.

Samples were cut into 3 × 3 mm. ribbons for accelerated aging tests. The shredded samples were heated in 80-gram portions in a circulating air oven for periods of 2, 4, 8, and 20 hours at 93° C. Intrinsic viscosity and benzene solubility were run on the aged samples, both before and after samples were milled (3 to 6 passes) in preparation for Mooney viscosity measurements. For deter-

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 41, No. 10, pages 2270–2272, October 1949
This work was done in connection with the Government research program on synthetic rubber, under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation.

mination of benzene solubility, an accurately weighed sample of about 0.2 gram of finely cut polymer was placed in a bottle and 100 cc. of benzene added. The stoppered bottle was allowed to stand for 22 hours in the dark, with occasional gentle swirling. After filtering the solution through 100-mesh screen, the concentration was determined by evaporation of the solvent from a 10-cc. portion of the filtrate. Viscosities of dilute benzene solutions containing 0.1 to 0.2 gram of polymer per 100 cc. of solution were measured at 25° C, with an Ostwald-Fenske viscometer. The intrinsic viscosity values recorded in Tables I and II should be termed inherent flow time if the conventions recommended by Cragg[2] are followed.

TABLE I

EFFECT OF ANTIOXIDANT ON RETENTION OF POLYMER PROPERTIES AFTER DRYING

Antioxidant content (%)	Drying conditions[a]	Intrinsic viscosity	Benzene solubility (%)
None	Air	1.05	73
	Vacuum	1.59	100
0.01	Air	1.32	99
	Vacuum	1.56	100
0.1	Air	1.56	100
	Vacuum	1.60	100

[a] Air drying 11 hours at 88° C; vacuum drying 20 hours at 60° C.

TABLE II

EFFECT OF ANTIOXIDANT ON RETENTION OF POLYMER PROPERTIES DURING ACCELERATED AGING

Antioxidant content (%)	Air aging hr. at 93° C	Mooney (Large rotor 100° C)	Intrinsic viscosity		Benzene solubility (%)	
			Before milling	After milling (3–6 passes)	Before milling	After milling (3–6 passes)
None	0	54	1.05	1.05	73	77
	2	82	0.67	0.67	50	51
	4	90	0.72	0.67	46	47
	8	93	0.65	0.71	47	47
	20	104	0.64	0.69	37	42
0.01 PBNA	0	22	1.32	1.31	99	100
	2	19.5	1.29	1.23	96	100
	4	29	1.18	1.22	91	99
	8	35	1.15	1.23	82	89
	20	40	1.26	1.25	83	84
0.1 PBNA	0	33	1.56	1.54	100	100
	2	33	1.56	1.54	100	100
	4	32	1.54	1.53	100	100
	8	31	1.48	1.47	100	100
	20	27	1.45	1.41	100	100
Standard GR-S 1.25 PBNA	0	44	1.81	1.81	100	100
	2	45	1.83	1.80	100	100
	4	45	1.80	1.81	100	100
	8	46	1.81	1.78	100	100
	20	41	1.68	1.69	100	100

Oxygen absorption measurements on crude GR-S are complicated by the necessity for maintaining a sample with a large surface area in a vertical position. In the range 90° to 100° C, GR-S usually softens during the initial stages of oxidation to a point where the polymer does not support its own weight.

The sample may drop from the support forming a thick sample, with attendant errors due to limited diffusion of oxygen. To minimize these difficulties, a layer of GR-S 0.1 mm. thick or less was deposited on the outer surface of a 15 × 2.5 cm. Pyrex test-tube by dipping in a benzene solution. For this purpose a 12 per cent solution was prepared by placing 12 grams of polymer and 88 cc. benzene in a screw-cap bottle and rotating overnight. The bottle was swept out with nitrogen before closing. Samples containing weak gel were rendered soluble by milling. With careful manipulation, a film weighing about 1 gram could be obtained with a single dip. After removal from the solution, the test-tube was rotated in a horizontal position until the film adhered to the glass. After standing a short time to allow most of the solvent to evaporate, the remaining solvent was removed under vacuum at room temperature. The weighed samples were stored in darkness under oxygen-free nitrogen. Oxygen absorption was measured at 70° C in oxygen at atmospheric pressure employing a method described by Shelton and Winn[3].

STABILITY OF GR-S AT ELEVATED TEMPERATURES

GR-S latex was prepared in the laboratory, with special precautions to prevent contamination by antioxidants. The required amount of phenyl-β-naphthylamine was carefully added to give samples containing 0.01 and 0.1 per cent of the antioxidant. A portion of the original latex was retained for an antioxidant-free control. After coagulation, the samples were divided. One series was air dried for 11 hours at 88° C. Another series was vacuum dried at 60° C in a system swept out with oxygen-free nitrogen.

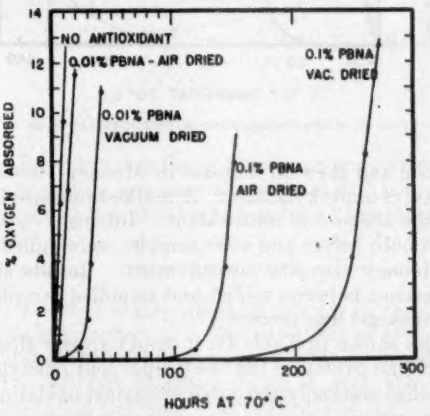


FIG. 1.—Oxygen absorption *vs.* antioxidant content. Effect of air drying.

To determine whether the drying operation had any effect on the polymer properties, the air-dried samples were compared with the corresponding vacuum-dried samples, with respect to intrinsic viscosity and benzene solubility. The results given in Table I show that air drying has produced changes in solubility and viscosity. In the absence of antioxidant, partial gelation occurred with the usual decrease in viscosity. With 0.01 per cent phenyl-β-naphthylamine, only a trace of gel and a slight decrease in viscosity were noted. No change in polymer properties was found when the antioxidant content was increased to

0.1 per cent. Mooney viscosity values for air-dried samples were 54, 22, and 33, respectively, for an antioxidant content of 0, 0.01, and 0.1 per cent. From these data it is clear that air drying has brought about changes in the polymer properties in the absence of antioxidant. Even under the rather severe drying conditions employed, significant protection against oxidation was afforded by traces of antioxidant.

The effect of further heating in air at 93° C is shown in Table II. The sample containing 0.1 per cent phenyl-β-naphthylamine remained completely soluble, and only slight changes in intrinsic viscosity or Mooney viscosity were noted. Similar results were observed with standard GR-S. In the presence of 0.01 per cent phenyl-β-naphthylamine, the solubility decreased as heating was continued, but the gel content was always less than for the antioxidant-free

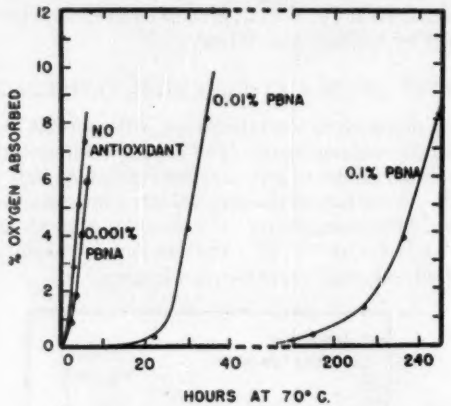


FIG. 2.—Oxygen absorption vs. antioxidant content.

control. A decrease and then an increase in Mooney viscosity occurred with 0.01 per cent phenyl-β-naphthylamine. A marked increase in Mooney viscosity was found in the absence of anitoxidant. Intrinsic viscosity and benzene solubility were run both before and after samples were milled (3 to 6 passes) in preparation for Mooney viscosity measurement. Results shown in Table II indicate little difference between milled and unmilled samples except where a small amount of weak gel was present.

From the results shown in Table II, it would appear that antioxidant-free GR-S readily undergoes oxidation but the 0.1 per cent phenyl-β-naphthylamine is sufficient to stabilize markedly the polymer against oxidation. To substantiate this conclusion, oxygen absorption measurements were made in oxygen at 70° C. Results are shown in Figure 1. Oxygen absorption was very rapid in the absence of antioxidant. The absorption rate was decreased somewhat for an antioxidant content of 0.01 per cent and markedly decreased when the concentration was increased to 0.1 per cent. In every case the vacuum-dried samples oxidized less rapidly than the air-dried samples. This difference was probably the result of consumption of part of the antioxidant during the drying operation. The reliability of these data was confirmed by repetition of the oxygen absorption measurements. Thus, the marked effect of traces of antioxidant on the stability of the polymer is clearly demonstrated by both oxygen

absorption measurements and by evaluation of changes in physical properties of the polymer.

To determine the minimum antioxidant concentration which would inhibit the oxidation reaction, the oxygen absorption of a sample containing only 0.001 per cent phenyl-β-naphthylamine was measured and compared with the control. At this concentration a slight but definite decrease in the oxygen absorption rate was noted. In Figure 2 oxygen absorption is shown as a function of antioxidant concentration. The samples employed had been dried at reduced pressure in oxygen-free nitrogen to eliminate any consumption of antioxidant during the drying process. From the shape of the curves it appears that the minimum effective concentration is about 0.001 per cent at 70° C. In Figure 3 the oxygen absorption rate of a commercial GR-S sample containing

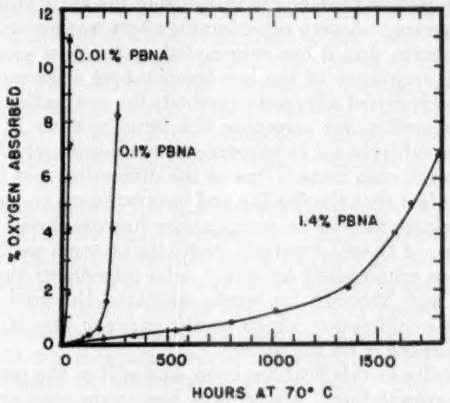


FIG. 3.—Oxygen absorption vs. antioxidant content.

1.4 per cent phenyl-β-naphthylamine is shown for comparison. At this concentration oxygen absorption was very slow; about 800 hours was required to absorb 1 per cent oxygen as compared with less than 2 hours for the antioxidant-free control.

CONCLUSIONS

Antioxidant-free GR-S is highly unstable toward oxygen. The inhibiting effect of phenyl-β-naphthylamine at a concentration as low as 0.001 per cent could be detected, and the effect became appreciable at an antioxidant content of 0.1 per cent. The activity of antioxidants at such low concentrations is difficult to explain except on the basis that the antioxidant functions as a chain terminating agent[4]. Under the usual conditions of processing or storage, the concentration of antioxidant commonly employed in production of GR-S, 1.25 to 1.5 per cent, appears entirely adequate. When used as criteria of polymer stability, satisfactory correlation was noted between oxygen absorption and deterioration of physical properties.

REFERENCES

[1] Dunbrook, *India Rubber World* **117**, 204 (1947).
[2] Cragg, *J. Colloid Science* **1**, 267 (1946).
[3] Shelton and Winn, *Ind. Eng. Chem.* **38**, 71 (1946).
[4] Cole and Field, *Ind. Eng. Chem.* **39**, 179 (1947).

THE EVALUATION OF FLEX-LIFE AND HEAT BUILD-UP PROPERTIES OF ELASTOMERS *

E. B. STOREY

POLYMER CORPORATION LIMITED, SARNIA, ONTARIO, CANADA

The deficiencies of the general-purpose polymer, GR-S in flex crack-growth and hysteresis properties became evident during the early stages of its production in North America. A very considerable effort was expended on this phase of the rubber program, and it has culminated, in the past year, in the increase flex crack-growth resistance of the low-temperature elastomers. During this period the development of adequate methods for evaluating the flex life and heat build-up properties, for screening the large number of pilot-plant elastomers, has given valuable aid in selecting new products which merited a fuller examination through road tests. One of the difficulties met in this evaluation arose through the fact that the flex life and heat build-up are opposed properties of a vulcanized elastomer. The compounder has developed methods for improving either one of these properties, but only at some sacrifice in the other. This situation was emphasized by Juve[1], who introduced the term "flex-hysteresis balance" and, through his work, indicated the goal for an improved elastomer, *i.e.*, a modification which would improve one of these properties, with no deleterious effect on the other.

A major difficulty in this field has been, and still is, the poor reproducibility of the flex crack-growth test. There have been numerous articles devoted to this subject[2], which have indicated the importance of the type of initial cut[3] and the temperature[4], while others have outlined statistical methods of evaluating replicate test data[5]. All these papers have pointed out the wide variation in results which has limited this test to a rough determination of the flex crack-growth properties. The measurement of the heat build-up of vulcanizates by means of the Goodrich flexometer[6], is a much more reproducible test, and there has not been any great incentive to reduce the variables introduced by differences in the state of cure of the test-specimens.

In the recent paper by Juve[1], the relationship between the flex life and heat build-up was presented as a relatively broad band in which the flex-hysteresis ratios for GR-S could be located, regardless of the recipe or state of cure of the vulcanizate. While recognition of the exact nature of the problem was a large step forward, the reproducibility of the laboratory tests was such that only a large improvement in either property could be detected in a reliable manner. This was undoubtedly a drawback when the large number of variables involved in polymerization could not be properly analyzed, and it hindered the steady advance towards a solution of the problem.

The production of experimental elastomers in a pilot plant incurs a considerable expense in time and material, so the need of a reliable test procedure for limited quantities of elastomer is evident. The development of micro tech-

* Reprinted from *The Rubber Age* (New York), Vol. 66, No. 6, pages 653–658, March 1950. This paper was presented before the Division of Rubber of the Chemical Institute of Canada, Hamilton, Ontario, June 10, 1949.

niques for stress-strain, rebound, etc., has been outlined by Garvey[7]. The lack of reproducibility of the flex crack-growth determination has not allowed its use on a microscale, and left no recourse except by use of replicate tests involving a relatively large quantity of material.

This dificiency has been investigated in the Research and Development Division, Polymer Corporation, Sarnia, and this paper gives an outline of the progress made in this field.

EXPERIMENTAL PROCEDURE

Flex crack-growth test.—The flex crack-growth test was carried out with the A.S.T.M. test-specimen[8] in a Wendes flex machine. This specimen, 6 by 1 by ¼-inch thick, has a $\frac{3}{16}$-inch diameter, semicircular groove molded into the surface, the center which runs at right-angles to its length. The specimen was clamped in the jaws of the Wendes flex machine, over a distance of one inch from each end, and then bent through an angle of 180°, and back to its original position, at a rate of 400 cycles per minute. A spacing device, similar to that described by Ford[9], was used to locate the specimen in the jaws to ensure that the center of the groove was placed midway between the jaws and at the point of maximum flexure. The jaws of the machine, capable of holding 12 specimens at one time, were located in a circulating air cabinet at a controlled ambient temperature.

An initial cut was made at the mid-point of the groove by punching a spear-shaped knife completely through the specimen. This produced a slit, 0.05-inch long, in the surface of the vulcanizate, whose length was parallel to the sides of the groove. The specimen was given an initial flexing to start a crack growing in the vulcanizate from either end of the slit. This period was adjusted to develop a crack whose total length was between 0.15 and 0.20 inch, and the rate of crack growth was measured between this point and the time at which the crack reached a length of approximately 0.60 inch. The resistance of the vulcanizate was expressed as the flex-life, or the number of kilocycles necessary to develop a crack one inch in length.

Heat build-up test.—The heat build-up was determined on a Goodrich flexometer[10], using a test cylinder 0.7-inch in diameter and about one inch high. The cylinder was formed by piling up four discs obtained from either end of the flex strip with a 0.7-inch diameter cutter and a rotary drill press. The conditions used in the test were: load, 143 lbs. per sq. in.; stroke, 0.175 inch; speed, 1800 cycles per min.; ambient temperature, 100° F. The temperature of the cylinder was measured with a thermocouple situated at the base of the test cylinder, and the dynamic compression was measured each minute during the test. The heat build-up was taken as the temperature after 15 minutes running time minus the ambient temperature.

Flex strips.—The flex strips were vulcanized in a 12-cavity mold for periods of 40, 55, 65, 80, and 100 minutes at 292° F. Two test recipes were used in this work:

Recipe No.	1	2
Elastomer	400	400
EPC black	200	200
B.R.T. No. 7	20	20
Stearic acid	—	12
Zinc oxide	20	20
Mercaptobenzothiazole	6	6
Sulfur	8	8
	654	666

These compounds were prepared on a 6 by 12-inch mill according to the procedure given in the Specifications for Government Synthetic Rubbers. In most cases three batches were prepared and then blended together on a 10 by 20-inch mill for 10 minutes.

Calculations.—The regression equations (Table II) were calculated, by the method of least squares, to determine the straight line which showed the best fit with the experimental values. The flex life was related to the percentage initial dynamic compression, measured by the Goodrich flexometer test. The heat build-up was related to the height of the compressed test cylinder after 15 minutes running time in the Goodrich flexometer.

TEST METHOD

The method used in comparing the flex life and heat build-up properties of two elastomers may be illustrated by the test data obtained for a standard GR-S production lot (S-2964) and an experimental elastomer of the Buna S-3 type (T-443). The elastomers were compounded in Recipe 2, vulcanized to produce a number of flex strips and tested by the method described in the preceding section. The flex strips, produced in each mold-loading, were divided into two equal lots. The flex life of one lot was determined at an ambient temperature of 80° F; the other lot was tested at 130° F. The average test values for each cure are given in Table I.

TABLE I

AVERAGE TEST DATA

Cure at 292° F (min.)	Initial dynamic compression (%)	Flex life at 80° F (kcy./in.)	Flex life at 130° F (kcy./in.)	Compressed height of test cylinder (inch)	Heat build-up (° F)
		S-2964, Recipe No. 2			
40	14.9	106.8	34.0	0.754	89.5
55	12.6	64.4	24.3	0.826	73.5
65	9.3	53.4	16.9	0.852	67.0
80	8.3	42.4	12.9	0.867	64.0
100	6.5	31.5	10.3	0.871	59.0
		T-443, Recipe No. 2			
40	12.7	123.2	43.1	0.809	99.5
55	9.4	72.2	31.8	0.854	85.0
65	8.0	62.3	26.1	0.878	79.5
80	7.1	45.0	18.4	0.901	75.0
100	5.9	39.7	13.9	0.911	71.0

Calculated indices of T-443 (S-2964 = 100)

Cure at 292° F (min.)	Flex life at 80° F		Flex life at 130° F		Heat build-up	
	A	B	A	B	A	B
40	115	147	127	157	90	78
55	112	134	131	182	87	79
65	117	152	154	195	84	77
80	106	137	143	170	85	75
100	126	181	135	193	83	76
Average	115	150	138	180	86	77

A—based on equal time of cure. B—based on equal stiffness.

The flex life at 130° F was considerably less than that at 80° F, and it is evident, as has already been stated in the literature, that the temperature must be accurately controlled during the flex crack-growth test. The flex life and the

heat build-up both decreased with an increase in the time of cure. The flex life varied, not only between duplicate cures of the same compounded batch, but also between strips from the same mold-loading.

It seemed evident that even strict control of the temperature and the time of cure were not sufficient to ensure production of the same state of cure in the various mold cavities. The initial dynamic modulus (Figure 1), which was measured during the heat build-up test, showed a similar variation between flex strips. The flex strip is bent through a definite angle (180°) by the Wendes flex machine and the stress produced in the groove of the specimen, therefore,

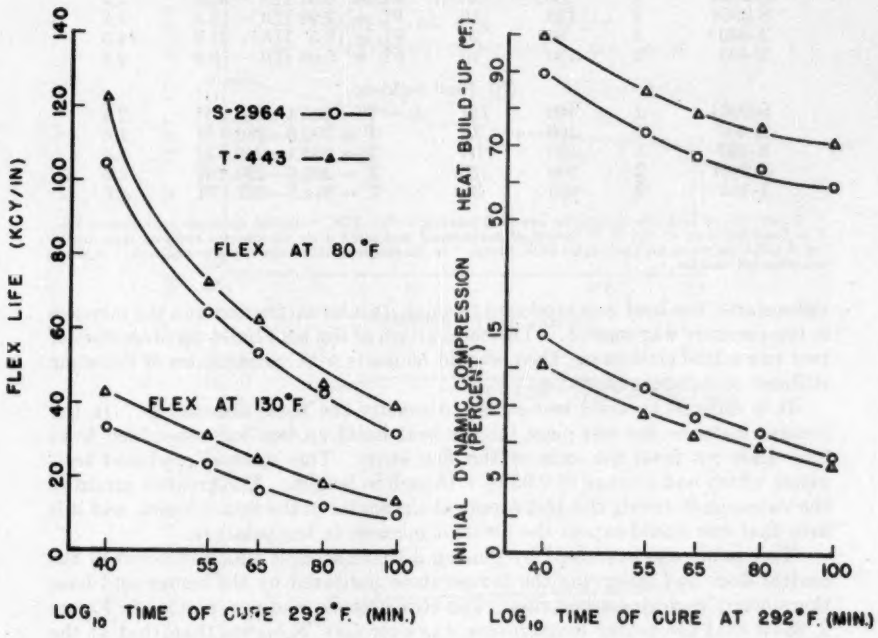


FIG. 1.

varies according to the stiffness of the vulcanizate. Since the rate of crack-growth varies with the stress placed on the end of the crack, a comparison of the flex life of two vulcanizates should be made under conditions of equal stress.

The stiffness of a vulcanizate increases with its state of cure and it might be expected that the flex life, for each flex strip, would depend on its state of cure. The initial dynamic modulus is a measure of the compression modulus or stiffness of the vulcanizate and should be proportional to the flex life of the vulcanizate. This relation was expressed in the form of the regression equation given in Table II. The observed variation in flex life of the different test strips vulcanized at the same time, then, corresponded to variations in the state of cure of the vulcanizate.

In the same way, the stiffness of the vulcanizate affected the results of the heat build-up test. The stiffer vulcanizate suffers less deformation in the Goodrich flexometer test, and, since a smaller amount of energy was imparted to the

TABLE II

REGRESSION EQUATIONS

Elastomer	Recipe number	Ambient temperature (° F)	Number of tests	Regression equation	Standard deviation of test results
			(A) Flex crack-growth		
S-2964 [1]	1	130	124	FL = 3.09 IDC—13.0	3.4
X-387	1	130	35	FL = 3.10 IDC—12.2	2.4
X-387[a]	1	130	40	FL = 2.06 IDC— 5.4	2.9
S-2964	2	80	20	FL = 9.07 IDC—31.5	7.7
S-2964	2	130	16	FL = 2.98 IDC—10.4	1.6
T-443 [2]	2	80	20	FL = 13.5 IDC—41.9	14.0
T-443	2	130	16	FL = 5.06 IDC—16.9	2.4
			(B) Heat build-up		
S-2964	1	100	117	T = 300.4—263.9 H	2.4
X-387	1	100	32	T = 300.6—266.0 H	1.6
X-387	1	100	36	T = 283.1—240.9 H	1.4
S-2964	2	100	27	T = 262.6—229.3 H	2.1
T-443	2	100	35	T = 314.5—267.1 H	1.7

Notes: FL = Flex life (kilocycles per inch crack-growth); IDC = Initial dynamic compression (%); T = Heat build-up (° F); H = Height of compressed test-piece after 15 minutes running time (inch): [1] = A GR-S polymer, production lot 2964, Sarnia; [2] = An experimental Buna S-3 type polymer; [a] = Single compounded batches.

vulcanizate, less heat was produced through its internal friction and the increase in temperature was smaller. The comparison of the heat build-up properties of two vulcanized elastomers, then, should be made with vulcanizates of the same stiffness or dynamic modulus.

It is difficult to mold test-pieces to exactly the same dimensions. In the present instance the test-piece for the heat build-up test was assembled from four discs cut from the ends of the flex strip. This method produced test-pieces which had a range of 0.95 to 1.15 inch in height. The greatest strain in the vulcanizate during this test occurs at the center of the test cylinder, and it is here that one would expect the greatest increase in temperature.

This point was examined by placing a thermocouple junction between the central discs and observing the temperature indicated by the center and base thermocouples during a test run. The temperature readings, plotted in Figure 2, show that the center temperature was over 100° F higher than that at the base of the test cylinder. The reading obtained at the base of the cylinder, then, is only an indication of the maximum temperature developed at the center of the cylinder.

It is evident that the heat conductivity and radiation of the vulcanizates must be assumed equal if the comparison is to be valid. The distance from the center to the base thermocouple must also be equal for a proper comparison, since this test showed a large temperature gradient through the sample, *i.e.*, at least 1° F per 0.005 inch. When the test cylinder is formed by cutting discs from the flex strip, it is inevitable that there will be variations in the original height of the cylinder.

The dimension that should be controlled is from the center to the base thermocouple at the time the heat build-up is measured, *i.e.*, in this case after 15 minutes' running time. The compressed height of the sample at this time may be measured with the Goodrich flexometer and, when expressed as a percentage, it is the final dynamic compression. This dimension was found to vary with the state of cure of the vulcanizate in the same way as the initial

dynamic compression. If the independent variable is selected as the compressed height of the test cylinder after 15 minutes' running time, allowance may be made for both variations in state of cure and the height of the test-cylinder by the one parameter. The relation between the heat build-up and the final compressed height was found to be a straight line, whose equation is given in Table II.

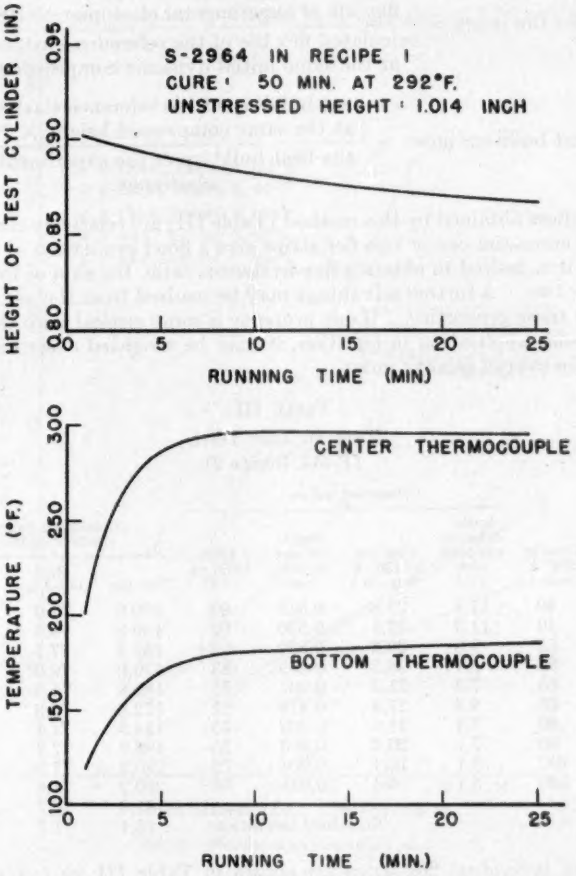


FIG. 2.

The flex life and heat build-up properties of an experimental elastomer may be compared to those of a reference elastomer for vulcanizates having the same stiffness. The stiffness of any vulcanizate is a measure of its state of cure and, hence, this method does not require a very strict control of either the time or temperature of vulcanization.

In the method, the experimental elastomer is compounded in the same recipe as the reference elastomer and vulcanized for a convenient time, which approximates the best tensile cure. The flex life and heat build-up are deter-

mined by the method described above, and the corresponding values for the reference elastomer are obtained from the regression equations by using the observed initial dynamic compression and final compressed height of the test specimen to calculate the corresponding values for the reference elastomer. The properties of the experimental elastomer may then be expressed as indices in the following manner:

$$\text{flex life index} = \frac{\text{flex life of experimental elastomer} \times 100}{\text{calculated flex life of the reference elastomer at the same initial dynamic compression.}}$$

$$\text{heat build-up index} = \frac{\text{heat build-up of the reference elastomer at the same compressed height} \times 100}{\text{the heat build-up of the experimental elastomer}}$$

The indices obtained by this method (Table III) are relatively constant over a series of cures and one or two flex strips give a good evaluation of the two indices. If it is desired to obtain a flex-hysteresis ratio, the sum of the indices is divided by two. A further advantage may be realized from the use of separate indices for these properties. If one property is more critical than the other for the particular application in question, it may be weighted accordingly in calculating the overall quality index.

TABLE III

TYPICAL TEST DATA

(T-443, Recipe 2)

		Observed values				Calculated indices (S-2964 = 100)		
Flex strip	Cure at 292° F (min.)	Initial dynamic compression (%)	Flex life at 130° F (kcy./in.)	Height of test cylinder (inch)	Heat build-up (° F)	Flex life	Heat build-up	Ratio
A	40	11.4	37.8	0.813	99	160.6	77.0	118.8
B	40	11.3	37.1	0.830	92	159.2	78.6	118.9
C	55	9.3	29.3	0.830	93	169.3	77.7	123.5
D	55	9.1	28.5	0.859	83	170.6	79.0	124.8
E	65	7.3	21.3	0.901	75	186.8	74.8	130.8
F	65	8.8	27.3	0.879	81	172.8	75.3	124.1
G	80	7.4	21.6	0.902	75	184.6	74.4	134.5
H	80	7.1	20.4	0.893	75	188.9	77.2	133.1
I	100	6.1	16.4	0.901	72	210.2	77.9	144.1
J	100	6.1	16.4	0.931	66	210.2	74.6	142.4
					Average	181.3	76.7	129.5
					Standard deviation	15.4	1.7	9.0

Data for individual flex-strips are shown in Table III for two elastomers produced under relatively different polymerization conditions and of a markedly different plasticity. The test cures ranged from under to over cures on these compounds, and the indices showed no variation that might not be accounted for by the normal error. In Table I similar data were calculated for the average values at each time of cure, and the comparison of the properties of the two elastomers was based on equal cure time as well as equal stiffness. The values based on equal cure time are quite different from those calculated for vulcanizates of equal stiffness. This result might be expected, as there is no reason why the rate of cure of the two elastomers should be equal.

This test procedure was carried out on 125 flex-strips of five different batches of S-2964, compounded in Recipe 1, and vulcanized for periods of 40, 55, 65, 80, and 100 minutes at 292° F. The data were expressed as two regression lines, whose equations are given in Table II. The deviation of each observed value from that given by the equation was used to calculate a standard deviation of the test. These values are also shown in Table II. The standard deviation of the flex crack-growth test, at an ambient temperature of 130° F, was 3.4 kilocycles per inch crack-growth, or a variation of 12.9 per cent when

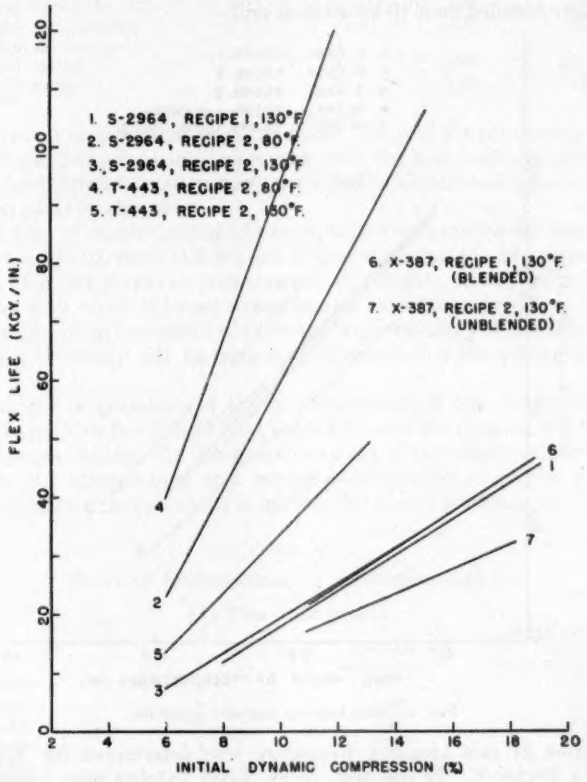


FIG. 3.—Flex-life regression equations.

based on the mean flex life for the series while that for the heat build-up test was 2.4° F, or a variation of 2.9 per cent.

The reproducibility of the flex crack-growth test is not very good, but this method, which relates the flex life with the state of cure of the vulcanizate, reduced the normal test error from about 20 to a little over 10 per cent.

The crack grows across the groove through the successive failure of small threads of vulcanizate upon which is concentrated a large portion of the stress produced by bending the flex-strip. This test is essentially different, then, from those which measure a particular property of the vulcanizate by placing the

stress, or strain, on a large mass of the vulcanizate. In the flex crack-growth test, therefore, the uniformity of the structure and composition of the vulcanizate play a very large part in determining the reproducibility of the test.

The effect of a number of variables on the flex crack-growth test have been observed in developing this test method. The ambient temperature has been shown to be a large factor in the test (Figure 1, Table I). The uniformity of the dispersion of the carbon black and other compounding ingredients also cause a large variation in the flex life. The method of compounding used in preparing the unvulcanized stock involved a refining step where three single batches were blended on a 10 by 20-inch mill.

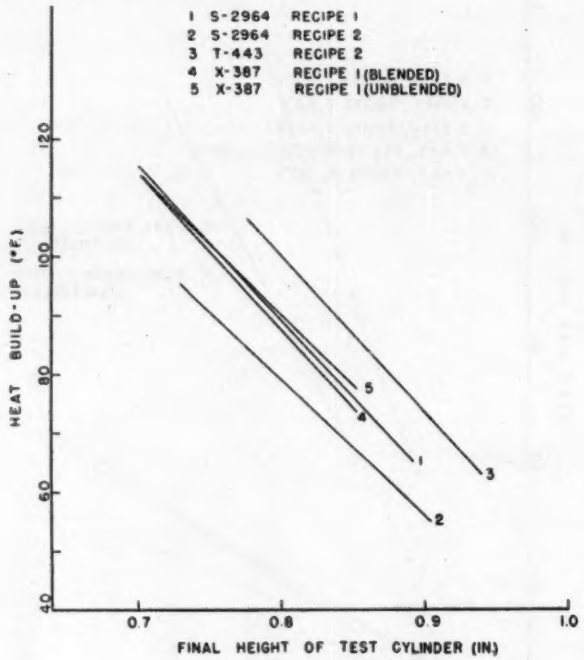


FIG. 4.—Heat build-up regression equations.

The effect of this blending procedure was determined for X-387, compounded in Recipe 1. In one test, three X-387 batches were blended on the mill; in the other, three single batches were vulcanized without the blending procedure. The equations calculated from the test results are given in Table II, and the calculated lines are shown on Figures 3 and 4. The heat build-up values were only slightly affected by the refining step, while this operation had a significant effect on the flex life. If the index for the unblended batches be denoted as 100, then, after blending, the flex-life index was 124 and the heat build-up index 104. The use of refining steps to produce an improvement in flex-life has been a farily common procedure in factory operations, and the improvement may be measured by this laboratory test.

The importance of a uniform dispersion of compounding ingredients, and the magnitude of the variation that may be introduced by any change in the com-

TABLE IV

EFFECT OF TEST VARIABLES

Test temperature	Flex life index 80° F	Flex life index 130° F	Heat build-up index 100° F
Effect of ambient temperature			
(a) S-2964, recipe 2	277	100	100
(b) T-443, recipe 2	305	100	100
Effect of blending compound			
(a) blended	—	124	104
(b) not blended	—	100	100
Effect of test recipe			
(a) recipe 1	—	100	100
(b) recipe 2	—	109	113

pounding procedure, is evident from the data. Tests of the properties of S-2964 in Recipes 1 and 2 showed some improvement in the heat build-up properties of Recipe 2, which differed from Recipe 1 only by the addition of 3 parts of stearic acid per 100 parts of elastomer.

The addition of stearic acid might be expected to improve the dispersion of the carbon black and, thus, the flex life of the vulcanizate. The improvement found in the flex life, however, was scarcely significant. A variation in stearic acid content may occur between experimental elastomers produced in a pilot plant, although not to the extent of three parts per hundred of elastomer. This factor, however, should not be neglected in comparing the properties of two elastomers.

The ambient temperature of the flex crack-growth test produced a slight change in the relative flex life indices (Table IV) over the range of 80° to 130° F. It might be expected that the comparative rating of two elastomers would vary according to the temperature, and careful consideration should be given that the most appropriate temperature is selected for such a comparison.

TABLE V

POINT OF INTERSECTION OF REGRESSION LINES

(A) Flex crack-growth

Elastomers	Recipe	Ambient temperature (° F)	Initial dynamic compression (%) (when calculated flex life is zero)
S-2964	1	130	4.19
X-387	1	130	3.95
X-387 [a]	1	130	2.62
S-2964	2	80	3.47
S-2964	2	130	3.49
T-443	2	80	3.11
T-443	2	130	3.36

(B) Heat build-up

Elastomers	Recipe	Ambient temperature (° F)	Height after 15 minutes' running time (inch) (when calculated heat build-up is zero)
S-2964	1	100	1.14
X-387	1	100	1.13
X-387 [a]	1	100	1.18
S-2964	2	100	1.15
T-443	2	100	1.18

[a] Single compounded batches, all others are three blended batches.

This method of comparing the flex-life properties of various elastomers gives a constant value, regardless of the state of cure of the vulcanizate, only if all the calculated regression lines have a common point of intersection at zero flex life. The same requirement must be met by the relations between the heat build-up and the height of the sample after 15 minutes' running time. The point of intersection of each regression line with the abscissa axis is given in Table V. These data further reflect the relative accuracy of the two tests and the sensitivity of the method to recipe variations. It would appear that the point of intersection of the regression lines in each test would be identical for different elastomers, providing that they were compounded in the same recipe and that the milling procedure produced an equivalent degree of dispersion of the ingredients.

SUMMARY

A method has been developed whereby the separate indices may be obtained for the flex life and heat build-up properties of elastomers. These indices are independent of the state of cure, but depend on the test recipe and the dispersion of the compounding ingredients. The method may be used to examine the effect of polymerization variables, compounding ingredients and procedures, or ambient temperature, on these two properties.

ACKNOWLEDGMENTS

The author wishes to acknowledge the support of the National Research Council, Ottawa, which made this work possible. The assistance and valid criticisms of N. R. Legge and S. C. Einhorn are greatly appreciated.

REFERENCES

[1] Juve, *Ind. Eng. Chem.* **39**, 1494 (1947).
[2] Carlton and Reinbold, *India Rubber World* **108**, 141 (1943); Holt and Knox, *Rubber Age* (N. Y.) **60**, 689 (1947); Morris and Ford, *Rubber Age* (N. Y.) **62**, 411 (1948).
[3] Breckley, *Rubber Age* (N. Y.) **53**, 331 (1943); Morris and Ford, *Rubber Age* (N. Y.) **62**, 411 (1948).
[4] Carlton and Reinbold, *India Rubber World* **108**, 141 (1943); Juve, *Ind. Eng. Chem.* **39**, 1494 (1947).
[5] Newton, *Trans. Inst. Rubber Ind.* **15**, 172 (1939); Stevens, *India Rubber World* **102**, 36 (1940).
[6] Lessig, *Ind. Eng. Chem. Anal. Ed.* **9**, 582 (1937).
[7] Garvey, *Ind. Eng. Chem.* **34**, 1320 (1942).
[8] American Society for Testing Materials, Book of A.S.T.M. Standards, **1946**, Section III-B, Method D-813-44T, p. 1011.
[9] American Society for Testing Materials, Book of A.S.T.M. Standards, **1946**, Section III-B, Method D-623-41T, Method A, p. 1003.

DYNAMIC COMPRESSION TEST FOR ADHESION OF RUBBER TO CORD FABRIC *

G. A. PITTMAN AND E. R. THORNLEY

HENLEY'S TYRE AND RUBBER CO., LTD., GRAVESEND, KENT, ENGLAND

During the last ten years or so, considerable attention has been paid to the problem of obtaining a satisfactory bond in the tire casing between the rubber and the cord fabric. The need for studying this problem has, of course, been intensified by the introduction of rayon fabric, and by the development of other new types of tire cord which require special bonding treatment. As is indicated by the several papers which have been published on the subject, various attempts have been made during this period to develop a laboratory adhesion test which would be suitable for general research purposes. These include the Goodrich compression cylinder method[1] and the Goodyear H test[2], both of which measure the strength of the initial bond formed between the cord and rubber. More particularly, reference should be made to the I.G. test used at Leverkusen[3], which measures the rate of breakdown of the bond under a dynamic treatment in which the sample is subjected to a longitudinal vibrating movement. Use has also been made of standard flexing machines for evaluating rubber to fabric bonds[4].

A test of this kind has been in use in the laboratories of Henley's Tyre and Rubber Co., Ltd., since 1937, and has proved of considerable value as a research method. Like the I.G. test, the Henley test consists essentially in examining the rate of breakdown of the bond obtained between a single cord and its surrounding compound when the cord-rubber structure is subjected to dynamic stressing.

Description of test.—The test-piece consists essentially of a single cord approximately 18 inches long, the middle 4 inch portion of which is bonded to rubber. In the standard test the rubber casing compound, with which the cord is treated, is built up round the cord into the form of a cylinder and molded to give an inner core $\frac{1}{8}$ inch in diameter, a semicure being applied at this stage. A sheath of standard compound is then built round the inner core, and finally molded to form a fully cured cylinder $\frac{1}{2}$ inch in diameter, having end flanges to enable the test-piece to be mounted in the separation machine (see Figure 1A).

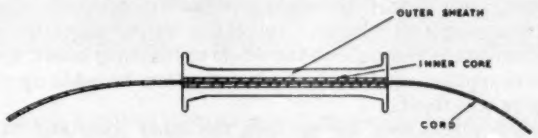


FIG. 1A.—Details of test-sample.

The purpose of this outer sheath is simply to form a medium through which the forces acting on the cord and its surrounding casing rubber may be conveniently transmitted.

* Reprinted from the Transactions of the *Institution of the Rubber Industry*, Vol. 25, No. 2, pages 116–129, August 1949.

The details of the method used for preparing these test-pieces may vary according to the circumstances of the test. In some cases, for example, untreated cords, or cords which have been dipped either in the laboratory or in the factory, may be rubberized in the laboratory, the casing rubber forming the inner core being applied in the form of a freshly calendered sheet which is built round the cord by hand. In other cases this inner core may be prepared by taking samples of cord which have been completely rubberized in the factory, and in such cases a single cord is carefully separated from the sample in such a way that the rubber immediately around the middle portion of the cord is left undisturbed. This rubber is then built up with additional casing rubber in a form suitable for molding the inner core. The object of using a separate inner

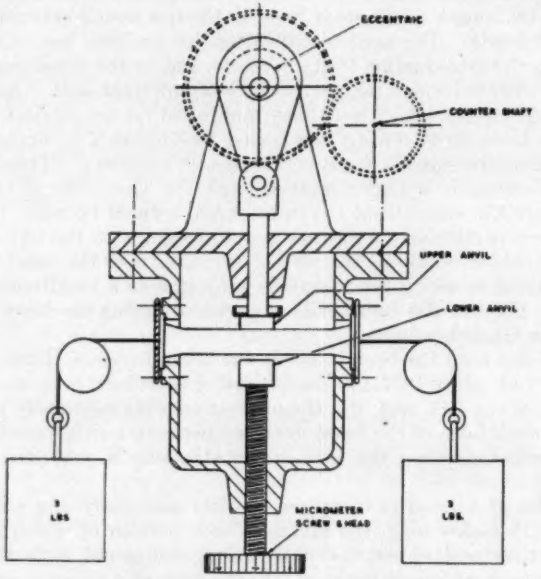


FIG. 1B.—Diagrammatic layout of cord separation machine.

core is, of course, to provide for the fact that there are cases where the casing rubber will be varied throughout the experiment. In such cases it is desirable that the outer sheath forming the main thickness of the test-piece should remain unchanged, even though the casing rubber immediately adjacent to the cord varies from sample to sample. In certain cases, where the casing compound remains constant throughout the whole of the experiment, the use of this inner core can be omitted, and the test-piece can then be made up entirely from the casing compound itself.

The two-piece molds used for molding the inner cores and the final test-pieces are of orthodox design, and in each case a channel is cut in the ends of the mold to allow the free ends of the cord to be led out of the mold. During the molding both of the inner core and of the final test-piece, a 3-lb. weight is applied to each end of the cord, so that the latter is held in tension during the molding operations. A molding pressure on the mold face of 600 lb. per sq. in. has been standardized for the test. (Experiments have indicated that the test

result is not measurably affected by varying this molding pressure over the range 300 to 1000 lb. per sq. in. As the pressure is allowed to fall below 300 lb. per sq. in., the results tend to become more and more erratic, while, at pressures much above 1000 lb. per sq. in., difficulties are experienced as a result of the displacement of the cord away from the center line of the test-piece and of the tendency for the cord to break during molding.)

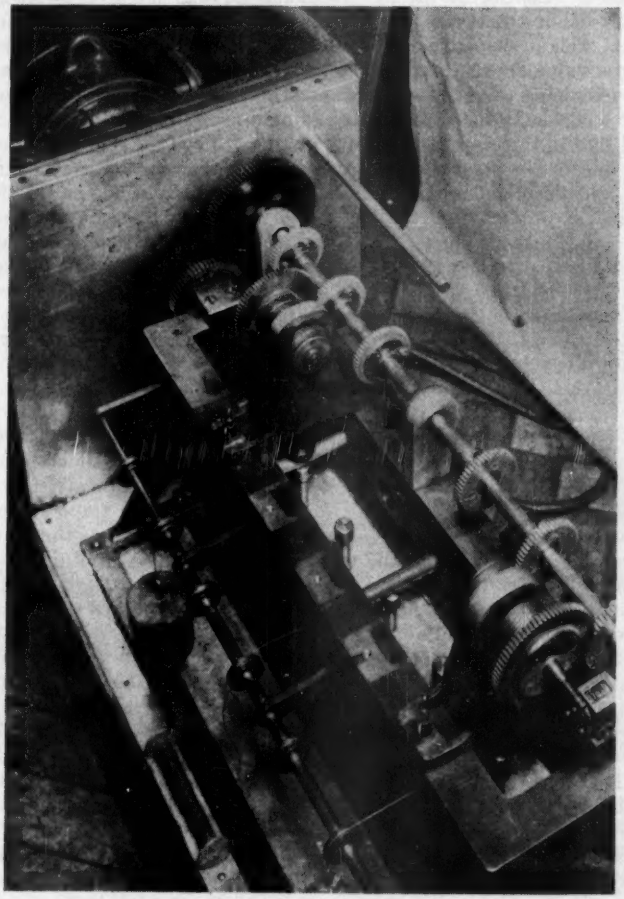


FIG. 2.

The test-pieces are then treated in a dynamic cord-adhesion test machine, the general principles of which are shown diagrammatically in Figure 1B. The machine consists essentially of a plunger $\frac{5}{8}$ inch in diameter, which is given a vertical movement of $\frac{1}{4}$ inch by an eccentric and connecting rod, and a stationary anvil of the same dimensions as the plunger. The eccentric is rotated by a motor at a speed of 430 r.p.m., i.e., at a speed generally in line with giant tire running speeds. The test-piece is located so that its center portion lies between

the plunger and the anvil, and is just in contact with the plunger when the latter is at the top of its stroke. Thus, the first part of the stroke of the plunger serves to bend the test-piece until it comes in contact with the anvil, and the second part compresses the sample. The position of the anvil is adjustable so that when it is at its lowest position the test-piece is subjected only to bending, while at the other extreme no bending occurs, and the test-piece is compressed by 0.25 inch. For normal use the machine is set to give both bending and compression. While the test is proceeding, the cord is maintained under tension by a 3-lb. weight suspended from each end, and the ambient temperature is raised to a value approximating to normal running conditions in a tire.

The machine is designed to simulate as accurately as possible the conditions to which a cord and the rubber surrounding it are subjected in service, and it is believed that in this respect the test is unique. Thus the tension of the cord in the tire due to the steady inflation pressure is represented by the suspended weights, and the slight increase in cord tension, which occurs as the tire flexes under load, is produced by the bending of the sample by the plunger. This same bending also produces stresses in the rubber and at the rubber-cord boundary in a manner analogous to that obtaining in the crown and shoulder of a tire as it deflects under load. The compression of the sample between the plunger and anvil finally reproduces the effects of the direct load which is transmitted by way of the tread to the casing, in the crown and shoulder region. It is this factor which is primarily responsible for breaking down the bond.

To return to the mechanical details of the apparatus, the test-piece is held precisely in position under the plunger by rubber flanges at the ends of the test-piece, which are clamped by circular washers. This method of location was used in the first place because, in the prototype machine, which accommodated one test-piece only, the temperature of the test-piece was controlled by keeping the body of the machine full of water from a constant tmperature source. Water was used originally as the heating medium, since it was thought at that time that the outer sheath of the test-piece would deteriorate under the combined effects of high temperature and mechanical wear in the presence of air. Subsequently it was established that, with a suitable sheathing compound, air can be used satisfactorily, and in the final form of the machine, as illustrated in Figures 2 and 3, the whole of the working parts are enclosed in an insulated oven. Low temperature resistance heaters are mounted in a space under the machine, and air is circulated over these by a centrifugal impeller, and thence, by way of a slot in the base of the oven, over the whole machine. The impeller is mounted directly on the main motor shaft, and draws its air from the opposite end of the oven. It thus maintains a stream of air over all the test-samples at a temperature which is controlled by a thermostat. The present machine accommodates six test-pieces at one time, the six compressing heads being driven through gearing from a countershalft within the oven. By this arrangement each head can be removed separately without disturbing the driving mechanism. Since all the moving parts are within the oven, the problem of lubrication is a difficult one, and for this reason all the bearings are ball races, packed with a high melting-point lubricant, while Tufnol gears are used on the countershaft to drive brass ones on each head, a combination which has a long life with no lubrication. It is essential that rapid wear should not occur in the eccentric and connecting rod bearings or on the plunger slide, since very small errors in the effective stroke of the plungers have marked effects on the life of the test-piece.

In practice it is found that the outer sheath of the test-piece suffers some permanent deformation in the region of compression, and this has the effect of

reducing the forces acting on the cord and its adjacent rubber as the test proceeds. The technique which has been developed to overcome this difficulty is to remove the test-pieces from the machine every 24 hours, and to determine the permanent set which has taken place by means of a hand dial gauge. The anvils are then raised by the amount of this permanent set and the compression is thus retored to the original value. To facilitate this adjustment, the anvils are carried on micrometer screws which have calibrated heads on their lower ends, making possible adjustment and resetting to an accuracy of 0.001 inch.

At the end of the treatment in the machine, the degree of breakdown of the bond may be determined either qualitatively by cutting the test-piece through the middle and examining the section visually, or quantitatively by determin-

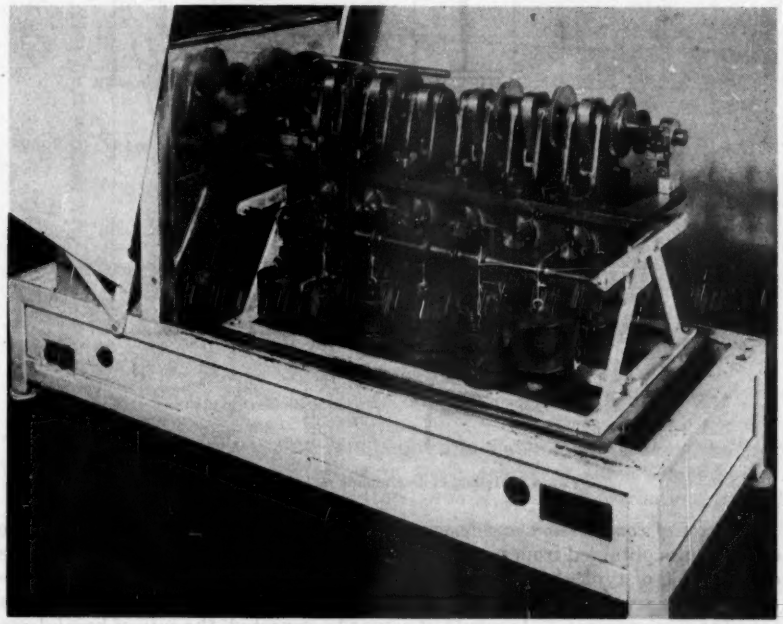


FIG. 3.

ing the load required to pull the cord through that portion of the test-piece coming underneath the plunger. In the latter case the rubber is removed from the cord after the treatment in the machine, except for a middle portion $\frac{1}{2}$ inch long, and the "pull-through" test is carried out in a tensile testing machine, the maximum reading being observed. Figure No. 4 illustrates the method adopted; the rubber bears up against a brass plate with a $\frac{1}{32}$-inch hole in the center. This plate is fastened to the lower grip of the tensile testing machine by a stirrup. The cord itself is held by the top grip of the machine and the bottom grip is traversed at a speed of 15 inches per minute.

In the full quantitative test procedure, pull-through loads are determined on test-pieces which have been treated for various periods in the machine, so that a curve may be drawn in which the pull-through load is plotted against the

time of test or number of compression cycles. Such a curve provides a useful picture of the breakdown of the bond, under the chosen test conditions, up to the point where a zero pull-through load is first obtained.

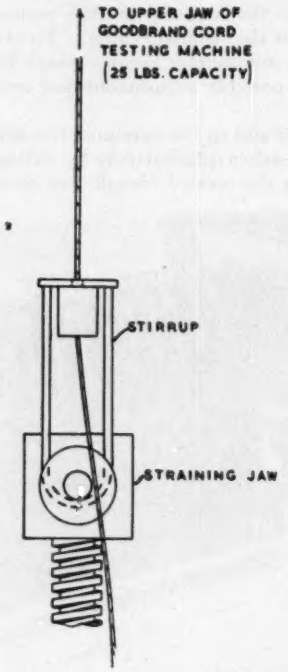


FIG. 4.—Method of determining pull through load.

Effects of compression and temperature.—In Figure 5 are reproduced some early results obtained from tests carried out in the original single head machine on a sample of typical cotton cord processed in the factory without dip treatment. The testing in the machine was carried out at 85° C, and through a range of compressions. As would of course be expected, the rate of breakdown increases rapidly as the amount of compression is increased. From a consideration of the stress strain relations operating in each case, a rough estimate may be obtained of the load required on the tire to produce the same amount of strain in the rubber immediately round the cord as is obtained with any given amount of compression applied to the test-piece. Thus, a test treatment carried out at 0.125 inch compression would correspond roughly with the treatment received in the shoulder region of a giant tire running under approximately 120 per cent normal full load. At a compression of 0.188 inch ($\frac{3}{16}$ inch) the corresponding load on the tire would be approximately 200 per cent normal full load. These are of course only approximations, the idea being to give a rough idea of what the test treatment means in terms of tire operating conditions. It will be noted that, according to the curves given in Figure 5, the rate of breakdown of the bond under test conditions which correspond with normal loading

in the tire is extremely low. This, of course, corresponds with the general behavior of untreated cotton cords in service.

As already indicated, the temperature at which the samples are treated in the test machine can be easily adjusted, and here again the test conditions can be made to line up with any set of conditions which might obtain in service. It is surprising to find that there is no pronounced temperature effect at any rate through the range 70° to 110° C covered by the tests so far carried out.

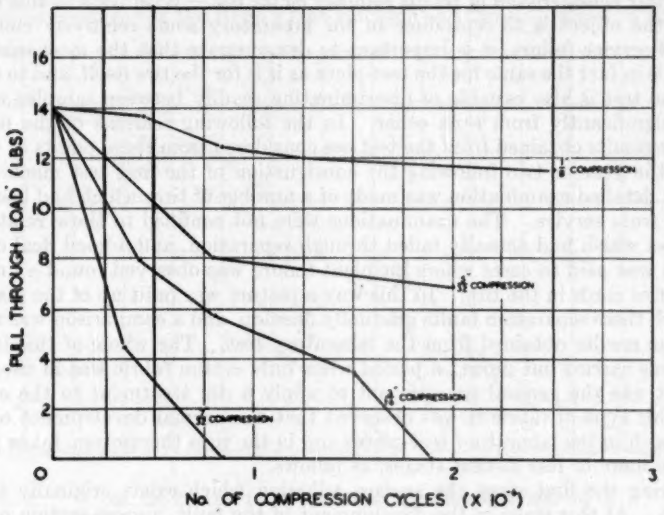


FIG. 5.—Rate of breakdown of rubber/cord bond at different compressions.

This is indicated by the typical results given in Table I, which show the drop in adhesion after two days' testing in the machine at three temperatures. These results were obtained with cotton cords of 22/5/3 construction, treated with a latex R.F. dope.

TABLE I

RATE OF BREAKDOWN OF RUBBER–CORD BOND AT DIFFERENT TEMPERATURES

	Pull-through load (carried out at room temp.)
No treatment in separation machine	13.0 lb.
2 days' treatment at 70° C and 0.14 inch compression	8.9 lb.
2 days' treatment at 90° C and 0.14 inch compression	9.1 lb.
2 days' treatment at 110° C and 0.14 inch compression	8.5 lb.

It is considered that this temperature effect requires further investigation. In the meantime a temperature of 70° C has been standardized for the test. The temperature referred to is the ambient temperature which is maintained while the test-piece is being subjected to the dynamic treatment in the test machine. The subsequent determination of the pull-through load is always carried out at room temperature. The pull-through test is merely employed to establish the final condition of the test-piece after any given treatment in the machine, and there appears, therefore, to be no reason why elevated temperatures should be used for this part of the test.

Accuracy of test.—The coefficient of variation obtained in repeated observations of the pull-through load after any given treatment in the machine is of the order of 5–7 per cent and, since at least eight test-pieces are used in carrying out the full test procedure, a sufficiently accurate picture can be obtained of the rate of breakdown of the bond. As with most tests carried out in the rubber laboratory, it is considered advisable to include a control with each set of samples tested at any time.

Further consideration of results obtained by the test.—With tests of this kind, where the object is to reproduce in the laboratory some relatively complex form of service failure, it is important to demonstrate that the mechanism of failure is in fact the same for the test-piece as it is for the tire itself, and to show that the test is also capable of discriminating readily between samples which differ significantly from each other. In the following sections of the paper, various results obtained from the test are considered from these points of view.

In the year or two following the construction of the first test machine in 1937, a detailed examination was made of a number of tires which had been returned from service. The examinations were not confined to those relatively few tires which had actually failed through separation, and a good deal of attention was paid to cases where incipient failure was observed round a limited number of cords in the tire. In this way a picture was built up of the manner in which these separation faults gradually develop, and a comparison was made with the results obtained from the laboratory test. The whole of this initial work was carried out during a period when only cotton fabric was in use, and when it was the general practice not to apply a dip treatment to the cords. With this type of fabric it was observed that the normal development of the fault, both in the laboratory test-pieces and in the tires themselves, takes place in three more or less distant stages, as follows.

During the first stage the surface adhesion which exists originally is destroyed. At this stage in the development of the fault, a cross-section of the cord and its surrounding rubber still appears to be perfectly intact until the rubber is stretched away from the cord, *e.g.*, with the point of a pin, when the absence of any surface bond is apparent. Judging by the number of cases noted during the examination of the tires referred to, where cords were seen to be in this condition, as compared with the few cases where complete separation had occurred, it was concluded that the breakdown of this purely surface adhesion takes place very early in the development of the fault, and that a cord in this state is still capable of standing up to normal running conditions without the fault necessarily developing much beyond this point. This conclusion was confirmed by the results of the laboratory tests, which indicate that the breakdown of the surface adhesion is obtained quite early in the test. At this stage in the development of the fault the cord is still tightly held in the rubber, the pull-through load having fallen only by about 15–20 per cent. In the test carried out at $\frac{1}{4}$ inch compression and 85° C shown in Figure 5, for example, complete breakdown of the surface bond was obtained after 1.5×10^6 cycles, *i.e.*, at the point A on the curve.

The second stage in the normal development of the fault, both in the tire and in the laboratory test-piece, consists of the gradual breakdown of the rubber which during the molding process has partly penetrated between the elements of the cord. This rubber is destroyed by a gradual process of attrition, until the cord eventually becomes perfectly loose (pull-through load = 0).

Finally, in the tire itself, as this process of attrition continues, the bridges of rubber between adjacent cords are broken down until ply separation proper

develops, and failure of the tire eventually occurs. This third and final stage is represented in the laboratory test-piece, at any rate when a fairly high compression is used, by an extension of the fault principally in the form of a tear, starting on each side of the cord, and developing in a plane at right-angles to the direction in which the test-piece is being compressed. Normally of course the testing is not taken beyond the end of the second stage.

From these comparisons carried out on tires and test-pieces prepared from undipped cotton cord, it was concluded that there is a close similarity between the failures produced in the Henley test machine and those obtained in service.

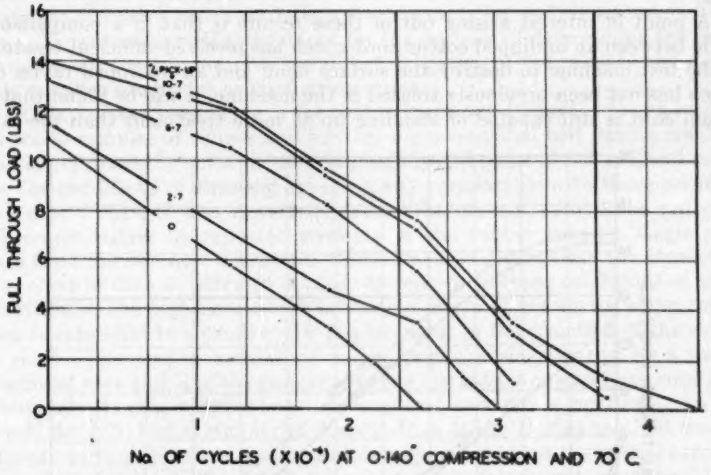


FIG. 6.—Effect on bond strength of treating cotton cords with increasing quantities of latex/R.F. resin adhesive.

The extent to which the test is capable of discriminating between processed cords of various types may be shown in the following examples, which have been chosen mainly because they relate to certain of the main developments in which tire manufacturers have been interested during and since the war. The tests were carried out on the present multiple-head machine illustrated in Figures 2 and 3, and, owing to minor differences in construction between this machine and the prototype machine, the results of these tests are on a somewhat different level to those previously referred to. It should also be noted that, in all the examples given, the casing compounds used were orthodox natural rubber compounds.

In Figure 6 are given the results of some early experiments carried out in the laboratory to determine the effect of treating cotton cords with an adhesive of the latex-resorcinol-formaldehyde resin type. The dope used in these experiments was the I.C.I. material, Vulcabond T. The cords, which were of 22/4/3 construction, were dipped in the laboratory in a dope of fairly low concentration, the number of dip treatments being varied from sample to sample so as to produce a series of samples with gradually increasing amounts of dope applied to the cord. The curves show that both the initial bond strength and the life of the test-piece in the machine are increased with increasing amounts of pick-up, and the discriminating power of the test in this particular case is well illustrated by its ability to reveal the effect of even small increases in the amount of dope applied.

Figure 7 gives composite curves based on fairly extensive test data in which comparisons are made between 2/1100 rayon cords and cotton cords of 22/4/3 construction. The results indicate clearly the poor adhesion obtained with undipped rayon cords when compared with that obtained with undipped cotton cords. In the case of the dipped cords, where the latex R.F. resin type of dope was used with a pick-up of 8 to 10 per cent, the rayon cords give slightly better adhesion on the whole than the cotton, and the effect of dipping on the rayon cord is even more striking than with the cotton cord. In general, this is in line with information obtained from wheel tests and from road performance data.

A point of interest arising out of these results is that, if a comparison is made between an undipped cotton cord which has received sufficient treatment in the test machine to destroy the surface bond and an undipped rayon cord which has not been previously treated in the machine, it will be found that the cotton cord is still capable of standing up to more treatment than the rayon

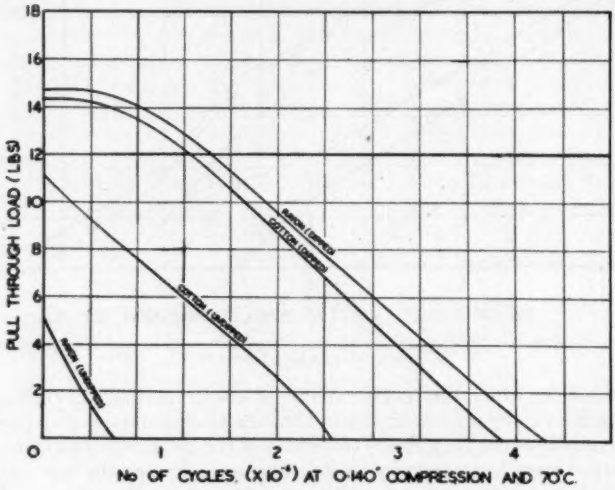


FIG. 7.—Comparisons between cotton and rayon.

cord; *i.e.*, it still requires longer treatment in the machine before a zero pull-through load is obtained. Now it must be assumed in the case of the cotton cord that, once the initial surface adhesion has been destroyed, there can no longer be any bond between the rubber and the cord due to the anchorage provided by the loose ends of the cotton fibers. It would appear, therefore, that the view commonly expressed that the poor adhesion obtained with undipped rayon cords is due to the absence of such loose fiber ends, cannot in fact completely explain the differences in the results obtained from the two types of cord.

Comparison of Henley test method with others.—The majority of tests which have been used for evaluating rubber-cord bonds have been of a static nature. The one most commonly used in the past has been the so-called ply stripping test, such as is described in A.S.T.M. D.413-39. There are two principal objections to this method. One is that it is most difficult to obtain uniform results and to keep the point of failure confined to the fabric-rubber boundary. The other lies in the poor discrimination which is obtained, owing to the fact that a

large percentage of the total force required to maintain the stripping action is spent in tearing the rubber elements which pass between the cords, so that changes in bond strength have little influence on the total load required to produce stripping.

Of recent years tests have been devised to overcome these objections by determining the load required to pull a cord lengthwise out of the surrounding rubber. The Goodyear H test measures this load directly, as does the pull-through test in the Henley method, while the Goodrich test takes as a measure of cord adhesion the axial compressive load required to produce bond failure in a cylinder of rubber which contains a single cord lying centrally across a diameter. These tests are all satisfactory for the purpose of determining the initial adhesion, but they do not give any direct indication of the rate of bond deterioration under conditions of fluctuating stress.

Attempts have been made in the past to carry out dynamic tests by running composite samples of rubber and cord on a conventional belt flexing machine. A difficulty arises, however, in determining the end point of the test, and in any case the conditions of stressing are in no way comparable with those occurring in service. The I.G. test, developed at Leverkusen, is the only known attempt to produce failure by repeated stressing of the rubber round a single cord, apart from the one now described. This machine differs from the Henley arrangement in that no attempt is made to reproduce those conditions of stress and strain in the test-piece which occur in a tire, but the surrounding rubber block is subjected to a small cyclic displacement in the direction of the axis of the cord. The cord is maintained under tension during the test by a weight hanging at each end, and the end point of the test is that at which the cord pulls through the rubber block when the weight at one end is removed. In this respect the I.G. test is simpler to operate than is the Henley method, since a complete test can be made on one sample only and without the special preparation and separate pull-through test involved in the latter. It is believed, however, that in the I.G. method there is some risk of the rate of breakdown of the bond being influenced, not only by the mechanical and thermal conditions which are imposed, but by oxidation and localized stress effects at the rubber-cord boundary in the region of the ends of the sample. Such effects do not influence the Henley test, owing to the use of a relatively long test-piece in which the center portion only is stressed and tested for bond. For these reasons it is considered that the Henley method is likely to be of greater value where a test is required for research purposes to give conditions as nearly as possible like those occurring in a tire.

SUMMARY

An improved laboratory method has been developed for the purpose of evaluating rubber-cord adhesions. The test-piece consists of a single cord surrounded by a thin cylindrical layer of casing compound which, in turn, is enclosed and protected by a thicker layer of rubber of standard composition. Such test-pieces are subjected to cyclic compression and bending, under controlled conditions of cord tension and ambient temperature, in a specially designed machine. The apparatus simulates the primary stresses and strains which occur in the crown and shoulder regions of a giant tire running under load, and it has been established that the cord bond in the test-pieces breaks down in a manner analogous to that in an overloaded tire. The degree of bond deterioration is determined by comparing the load required to pull the cord axially through that part of the rubber which has been subjected to compression

after a specific number of cycles with that required to do so in a similar untreated test-piece. Data show the rate at which the rubber-cord bond deteriorates with various degrees of compression and temperature, and examples are given of the use of the method for evaluating bonding agents for cotton and rayon cords. A general comparison is made between the Henley test and other adhesion tests known to be in use.

Acknowledgment.—The authors wish to thank Henley's Tyre & Rubber Co. Ltd. for permission to publish this paper. Thanks are also due to Messrs. W. T. Henley's Telegraph Works' Research Laboratories for valuable assistance in preparing the photographs for the paper.

REFERENCES

[1] Lessig and Compton, RUBBER CHEM. & TECHNOL. 19, 223 (1946).
[2] Lyons, Nelson and Conrad, U. S. Dept. of Agriculture, Bur. of Agricultural and Industrial Chemistry, Publication A.I.C.-99 (1945).
[3] Field Information Agency Technical, Final Report No. 722, "Synthetic Rubber Desmodur R", 1946.
[4] American Society for Testing Materials, Designation D430-40.

TACK OF BUTYL AND NATURAL RUBBERS *

R. K. Beckwith, L. M. Welch, and J. F. Nelson

Standard Oil Development Company, Elizabeth, N. J.

AND

A. L. Chaney and E. A. McCracken

Esso Standard Oil Company, Louisiana Division, Baton Rouge, La.

In the manufacture of Butyl inner tubes one of the major problems is the making of a satisfactory butt splice. The Goodyear splicing machine shown in the adjacent photographs is in general use in the industry for butt splicing. The tube lengths, which are cut somewhat longer than required, are placed in position by the operator as shown in Figure A. The splicing is then done automatically as follows. (1) The clamp arms close down upon the tube ends and flatten them into the clamp dies. (2) A pair of heated knives descend vertically onto a cutting anvil and trim off both tube ends, leaving clean and tacky faces ready for splicing together. (3) The knives and anvil then move out of the way (Figure B). (4) The clamps move horizontally toward each other, pressing forcibly together the two freshly cut tube ends and holding them so for a short interval of time. (5) Finally the clamps open up and return to their ready position (Figure C), completing the cycle. The timing and pressures of any operation in the cycle can be varied, but the full cycle completes a splice in about thirty seconds. While it has been clearly shown that mechanical improvements in the splicing machine are effective in reducing rejects at the butt splicer, there has been a general feeling that Butyl has a lower margin of safety for splicing than has natural rubber. Furthermore, it has been reported that Butyl shows quite erratic results in the splicing operation. In view of these difficulties, it was felt that a laboratory study of the factors influencing the tack of Butyl would be helpful in understanding the splicing problem. Since natural rubber is considered to have good tack, Butyl and natural rubber were compared under the same test conditions in so far as possible.

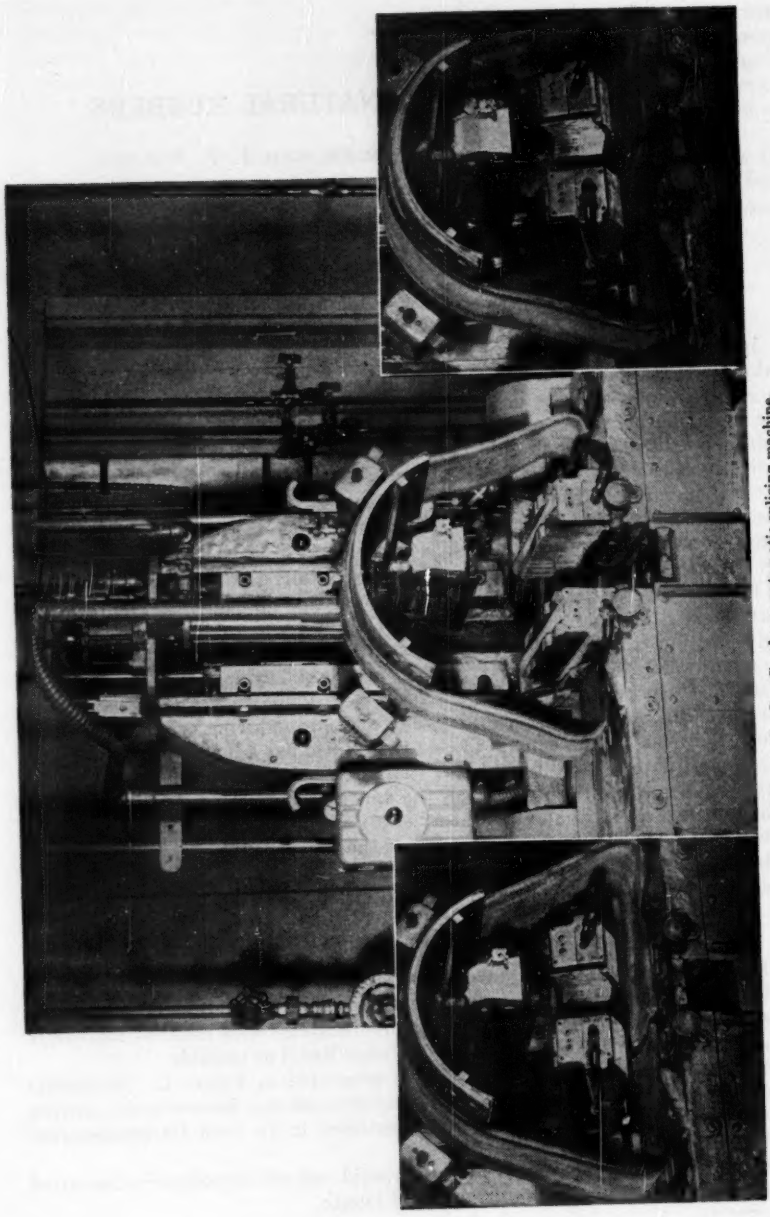
EXPERIMENTAL METHOD

The experimental technique which was used in this study is based on a method for quantitatively measuring tack in elastomers which was used by Busse, Lambert, and Verdery[1]. Certain modifications were made to contribute as much information to the problem of splicing Butyl as possible.

A diagrammatic sketch of the unit is presented in Figure 1. It consists essentially of a platform scale for measuring pressure and tension and a moving arm for contacting the rubber samples, enclosed in an oven for temperature and humidity control.

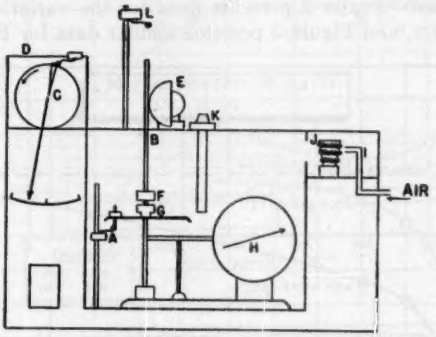
The samples are prepared by extruding solid rods of the polymer of required cross-section and cutting them to required length.

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 41, No. 10, pages 2247–2251, October 1949. This paper was presented before the Division of Rubber Chemistry at the 113th meeting of the American Chemical Society, Chicago, Illinois, April 19–23, 1948.



FIGS. A, B, C.—Goodyear automatic splicing machine.

The sample (usually 1.5 inches long × 0.25 inch diameter) is exposed between clamps. Clamps and sample are attached to machine, a slight tension is applied, and the sample is cut by hand. Hand switch is thrown starting automatic cycle. As contact between fresh cut surfaces is made, the balance pan is depressed, making contact with microswitch *A*, which stops any downward motion of mandril *B* when the predetermined pressure is reached, and turns on timer *C*. Timer *C* holds the sample under the predetermined stress for a predetermined time. Microswitch *D* then starts motor *E* in the reverse direction, thus separating clamps *F* and *G*. The maximum tension at the break point is read on scale *H*. Microswitch *L* turns unit off at the end of the cycle.



TACKMETER

FIG. 1.

Temperature and humidity may be controlled by air from line *I* blowing past cone heaters *J*. The entire unit is in an oven whose temperature is controlled by temperature regulator *K*. Time of contact from initial contacting through maximum pressure to initial tension is about 6 seconds. Rate of separation is variable.

When samples are spliced at temperatures other than room temperature, they are held at the temperature in the oven for 20 minutes so that equilibrium may be reached. Samples are cut with a razor edge at room temperature or with a knife electrically heated for cutting knife temperature studies.

The reproducibility of the data was better than expected; the average deviation was less than 10 per cent in most of the experiments, although at the critical points (where small changes in a variable have a large effect on the apparent tack strength) the deviation sometimes exceeded this value. In general, eight duplicate samples were run for each determination. The reproducibility between different determinations under identical conditions was somewhat less for Hevea than for Butyl because it is more difficult to prepare duplicate batches of Hevea.

Unless otherwise noted, the data presented are based on the following test conditions: contact time of 6 seconds, specimen at room temperature, and 10 inches per minute rate of pull. Other variables, such as contact pressure, compound, and knife temperature, are reported with each set of data.

For the purposes of this study, the tack strength of a polymer is considered to be the force required to separate two pieces of the same polymer after they have been contacted under a given set of conditions. The raw stock strength

is the comparable value obtained on an uncut sample of polymer. The relative tack strength is the ratio between the tack strength and the raw stock strength expressed in percentage.

The factors affecting the measured tack values have been divided as follows into three groups: external factors, the conditions under which the polymers are contacted and separated; inherent polymer factors, such as molecular weight, molecular weight distribution, and unsaturation; and compounding factors, including blacks, plasticizers, and accelerators.

EXTERNAL FACTORS

Contact pressure.—Figure 2 presents data for the variation of the tack of Butyl with pressure, and Figure 3 presents similar data for Hevea. The tack

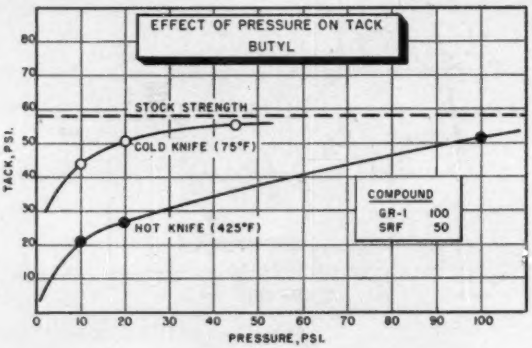


FIG. 2.

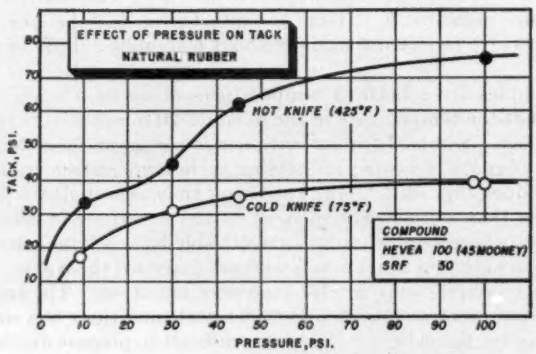


FIG. 3.

of Butyl rises sharply as the pressure rises to between 10 and 20 pounds per square inch; the tack then increases more slowly as the pressure is increased. When cut with a knife at room temperature, Butyl reaches its maximum tack strength below 50 pounds per square inch applied pressure. When cut with a hot knife (approximately 425° F), Butyl requires a pressure somewhat higher than 100 pounds per square inch before its maximum tack strength is reached.

Hevea, on the other hand, when cut with a knife at room temperature, has a tack strength which is lower than that of Butyl under the same conditions. However, if Hevea is cut with a hot knife (approximately 425° F) the tack strength rises sharply with increasing contact pressure. The upper limit of 80 pounds per square inch is the value at which the sample tore from the clamps, the true stock strength not being reached. When a hot knife is used for cutting, the tack strength of Hevea exceeds that of Butyl.

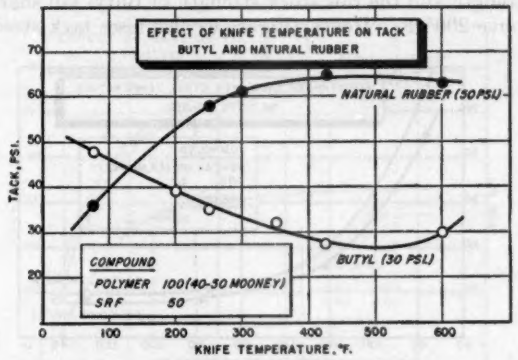


FIG. 4.

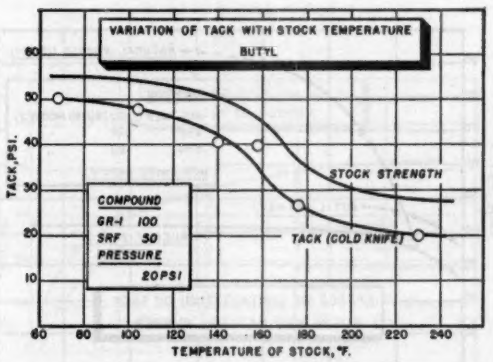


FIG. 5.

The effect of increasing pressure can be understood as an improvement of molecular contact, with a resultant increase in the effectiveness of molecular forces of attraction, and an increasing degree of intermingling of polymer chain segments. The effect of cutting knife temperature cannot be so readily explained. The following section offers additional data on this point.

Cutting knife temperature.—Figure 4 presents data for the effect of cutting knife temperature on the tack of Butyl and Hevea. The tests were conducted at pressures of 50 and 30 pounds per square inch for Hevea and Butyl, respectively. At these pressures the change of tack with pressure was relatively small. The tack of Butyl decreases regularly as the knife rises from 75° to 400° F, goes through a minimum at about 500° F, and appears to rise again as the knife

temperature reaches 600° F. The tack of Hevea increases rapidly as the knife temperature is increased up to about 300° F; further temperature rise has little effect in increasing tack. However, the limiting value for Hevea shown in Figure 4 may be due to clamp breaks as its ultimate stock strength could not be measured.

Polymer temperature.—As the temperature of the polymer rises, the tack strength decreases for both Butyl and Hevea. Figure 5 shows that, above 150° F, the tack strength and the raw stock strength of Butyl fall sharply, but tend to level off above 200° F. Hevea (Figure 6) also loses tack strength and raw

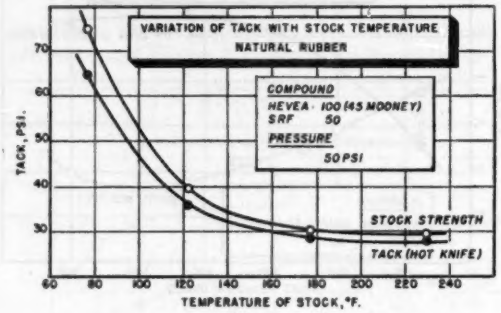


FIG. 6.

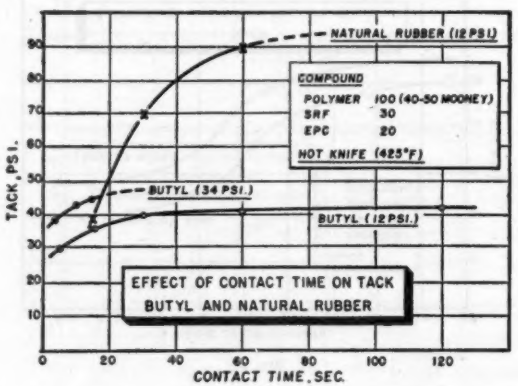


FIG. 7.

stock strength, the raw stock strength falling rapidly between 80° and 120° F, and then, with the tack strength, decreasing more slowly above that temperature.

At the higher temperatures used, the polymers had low raw stock strength and, therefore, yielded at a relatively low tension.

Time of contact.—Figure 7 presents the data for the effect of time of contact on tack strength. The tack strength of both Butyl and Hevea rises as the time of contact increases until the limiting stock strength is reached. At a higher pressure, Butyl reaches its limiting strength more rapidly and a similar effect

would be anticipated for Hevea. A greater length of time permits the flow to a greater extent, thereby improving molecular contact.

Rate of pull.—Figures 8 and 9 give the data for the effect of rate of pull on the apparent stock and tack strengths of Butyl and Hevea, respectively. For both polymers, the apparent tack strength increases as the rate of pull increases. The effect of cutting knife temperature is the same as previously noted. The relatively low tack shown for Hevea in Figure 9 results from the low black loading.

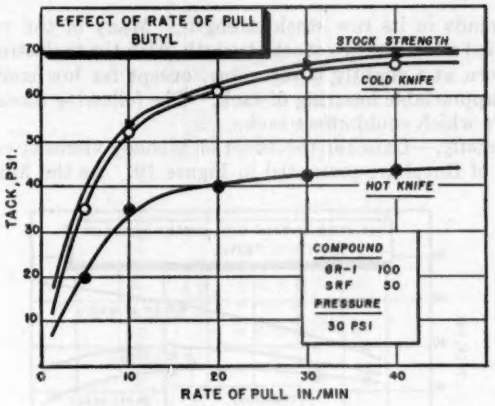


FIG. 8.

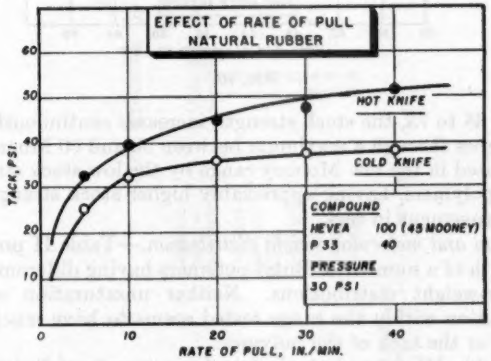


FIG. 9.

Humidity.—The data in Table I show that the tack strength of Butyl is virtually unaffected by humidity over a range of 25 to 90 per cent relative humidity.

INHERENT POLYMER FACTORS

Because the tack strength of Butyl lies within 85 to 95 per cent of the stock strength under ideal conditions (Figures 2, 5, and 8), there is little additional improvement that can be made in the tack strength of Butyl until some im-

TABLE I

EFFECT OF RELATIVE HUMIDITY ON TACK OF BUTYL

Test conditions		Relative humidity (%)	Tack (lb./sq. in.)
GR-I	100	26	57.5 ± 1.6
SRF	50	63	55.1 ± 1.2
Contact pressure (lb. per sq. in.)	30	91	55.0 ± 1.6
Knife temperature (° F)	75		

provement is made in its raw stock strength. Many of the variables which have been studied affect the raw stock strength, with the tack strength following the same pattern at a slightly lower value, except for low contact pressures, which give an appreciable lowering of tack. The following discussion concerns polymer factors which could affect tack.

Mooney viscosity.—Data for the effect of Mooney viscosity on the tack and stock strength of Butyl are presented in Figure 10. As the Mooney viscosity

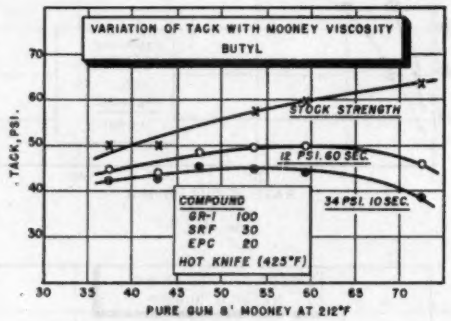


FIG. 10.

increases from 38 to 73, the stock strength increases continuously, whereas the tack strength goes through a maximum between 50 and 60 Mooney. The tack strength is limited in the low Mooney range by the low stock strength, but the high Mooney polymers, having appreciably higher stock strength, are subject to further improvement in tack.

Unsaturation and molecular weight distribution.—Table II presents the data for tack strength of a number of Butyl polymers having different unsaturations and molecular-weight distributions. Neither unsaturation nor molecular-weight distribution within the range tested seems to have much effect on the stock strength or the tack of the polymer.

Scorch.—Table III presents tack data for a sample of Butyl, compounded in an inner tube formulation, which has been quite scorched (precured), as indicated by the Williams plasticity. These show a surprisingly small loss of tack, even with the high degree of scorching obtained in this experiment. It is concluded that the mild scorching encountered in the processing of inner tubes does not appreciably affect the tack of the stock. However, scorching is undoubtedly harmful and does increase the splice rejects, since a scorched stock requires higher pressure in the performing operation; this puts more stress on the splice, which in turn may cause a failure, even though the splice on the machine is normal. The lowering of the tack of Butyl by high knife temperature (Figure

TABLE II

TACK STRENGTH OF VARIOUS BUTYL POLYMERS

Sample	Polymer	Relative mol. wt. distribution	Mole-% unsatd.	Mooney[a] viscosity at 100° C, 8 min.	Stock strength[b], (lb./sq. in.)	Tack strength[b,c]	
						60 sec. at 12 (lb./sq. in.)	10 sec. at 33.6 (lb./sq. in.)
1	GR-I	Normal	1.6	43	48.4 ± 1.3	44.7 ± 0.9	43.9 ± 1.3
2	R-3	Narrow	1.6	47	56.3 ± 1.4	49.2 ± 1.4	49.0 ± 1.4
3	R-4	Wide	1.6	46	51.1 ± 0.2	47.7 ± 0.5	45.9 ± 0.3
4	R-5	Very wide	1.6	43	60.1 ± 0.6	47.7 ± 0.4	46.0 ± 1.4
5	R-6	Wide	2.4	46	53.1 ± 0.5	46.8 ± 0.9	44.9 ± 0.7
6	Y-15	Normal	2.3	43	47.6 ± 0.6	45.2 ± 0.5	43.4 ± 0.6
7	Y-25	Normal	3.3	43	47.8 ± 0.2	44.0 ± 0.7	40.6 ± 0.7

[a] Pure gum.
[b] Based on original cross-sectional area.
[c] Compound: polymer 100, SRF 30, EPC 20; hot knife.

TABLE III

EFFECT OF SCORCH ON TACK STRENGTH OF GR-I TUBE STOCK

Extrusion time at 275° F (min.)[a]	Williams plasticity	Tack[b]	Formulation of stock	Parts
0.5	138–1	22.1 ± 0.9	Polymer, GR-I	100
2.0	136–3	22.0 ± 1.5	Black, SRF	50
4.0	137–2	20.4 ± 1.0	ZnO	5
6.0	145–3	20.3 ± 1.3	Sulfur	2
8.0	174–46	19.0 ± 1.0	Tuads	1
8.2	215–113	(19.0)	Captax	0.5

[a] Stock scorched by recycling through extruder.
[b] Pressure 10 lb./sq. in., contact time 6 sec., rate of pull 10 in./min.

4) is not attributed to scorch in the normal sense, because the presence or absence of curatives has little effect on this phenomenon.

COMPOUNDING FACTORS

Carbon black.—Table IV presents data for the effect of different types of carbon black on the apparent tack of Butyl. As the particle size of the carbon black increases, the stock strength and the tack strength both decrease. Two mixtures of different blacks have an effect which would be anticipated by interpolation between the values obtained for Butyl containing only the individual blacks in question. Since ratio of the tack strength to the stock strength is reasonably constant, it may be concluded that the type of carbon black affects the tack strength only in so far as it changes the raw stock strength.

TABLE IV

EFFECT OF CARBON BLACKS ON TACK OF BUTYL

Type of black[a]	Stock strength (lb./sq. in.)	Tack (lb./sq. in.)[b] 12 lb./sq. in. 30-min. contact	12 lb./sq. in. 60-min. contact	33.6 lb./sq. in., 10-min. contact
EPC (WYEX)	56.6	43.1	48.4	47.1
HMF (Philblack)	54.6	42.4	47.4	45.8
SRF (Gastex)	43.5	33.7	37.9	35.2
MT (Thermax)	38.1	30.3	34.9	33.1

[a] Formulation: GR-I 100, black 50.
[b] Rate of pull 13 in./min., hot knife.

Plasticizers.—Data for the effect of various plasticizers (3 parts per 100 parts gum) on the tack of Butyl are given in Table V. Of the plasticizers listed, only two seem to have a pronounced effect on the relative tack strength. Paraffin wax and stearic acid lower the tack of Butyl to less than 53 per cent and less than 65 per cent, respectively, of its inherent tack strength under the same conditions. None of the others raise the tack strength by a significant amount, although they alter the shape of the contact time or pressure against tack curve somewhat.

The raw stock strength is lowered about 10 per cent by Forum 20 and dibenzyl ether and about 15 per cent by paraffin wax and petrolatum. This decrease in stock strength is reflected in the absolute value of the tack strength, but only in case of paraffin is it also reflected in the relative tack strength.

TABLE V

EFFECT OF PLASTICIZERS ON TACK OF BUTYL

Plasticizer[a]	Stock strength (lb./sq. in.)	Tack[b] (12 lb./sq. in.) 30-min. contact lb./sq. in.	Tack[b] (12 lb./sq. in.) 30-min. contact Relative strength (%)	Tack[b] (12 lb./sq. in.) 60-min. contact lb./sq. in.	Tack[b] (12 lb./sq. in.) 60-min. contact Relative strength (%)	Tack[b] (33.6 lb./sq. in.), 10-min. contact lb./sq. in.	Tack[b] (33.6 lb./sq. in.), 10-min. contact Relative strength (%)
Glycerol	48.3 ± 0.4	36.6 ± 1.4	75.8	41.7 ± 0.8	86.3	41.1 ± 0.6	85.1
Forum 20	45.1 ± 0.2	33.6 ± 0.8	74.5	39.9 ± 1.3	88.5	39.1 ± 0.8	86.7
Petrolatum	42.5 ± 0.2	33.8 ± 0.9	79.6	36.7 ± 1.0	86.4	36.0 ± 0.9	84.7
Dibenzyl ether	44.6 ± 0.4	36.4 ± 1.3	81.6	39.8 ± 0.5	89.2	37.8 ± 0.8	84.8
Paraffin wax	42.0 ± 0.2	<16.3	<38.8	16.8 ± 0.4	40.0	17.3 ± 0.2	41.2
Aluminum stearate	50.8 ± 0.9	37.8 ± 0.6	74.4	42.5 ± 0.9	83.7	40.7 ± 0.5	80.1
Zinc stearate	50.1 ± 0.5	37.4 ± 0.5	74.7	42.9 ± 0.5	85.8	42.8 ± 0.5	85.4
Stearic acid	48.8 ± 0.6	22.9 ± 1.2	46.9	24.1 ± 0.5	49.4	31.7 ± 1.5	65.0
None	49.7 ± 0.2	36.3 ± 0.9	73.0	44.9 ± 0.6	90.3	39.5 ± 0.6	79.5

[a] Formulation (parts by weight): GR-I 100, SRF 30, EPC 20, plasticizer 3.
[b] Rate of pull 13 in./min., hot knife.

Stearic acid does not affect the raw stock strength, but does lower the relative tack strength as noted above.

SUMMARY

A comparative study of the tack of Butyl and natural rubbers was made by contacting freshly cut surfaces of the compounds under various time-temperature-pressure conditions and measuring the force required to separate the splice. The temperature of the knife used to cut the samples was found to be of primary importance. The tack of Butyl compounded with 50 parts of semireënforcing carbon black (no curatives) decreases regularly with increasing knife temperature. Both longer time and higher pressure of contact favor better splicing. Data are presented on the effect of various plasticizers and carbon blacks on the tack of Butyl compounds.

REFERENCE

[1] Busse, Lambert, and Verdery, *J. Applied Physics* **17**, 376 (1946).

RUBBER BONDING *

J. M. Buist and W. J. S. Naunton

Rubber Service Laboratories, Imperial Chemical Industries, Ltd., Blackley, Manchester, England

Bonding in this paper is limited to the formation of bonds of considerable strength, and little attention is paid to the numerous agents which can be used for sticking rubber (usually cured rubber) to various materials. For many purposes a good stick, such as that obtained by the use of cyclized rubber, is sufficient, especially where service conditions tend to maintain the bond rather than to break it.

Two other aspects of bonding, namely, bonding by brass-plating and the discussion of the nature of the bond do not enter into the subject matter of this paper. Brass-plating is a whole subject in itself, and is of technical interest only to those who have sufficient bonding work to maintain a plating unit in active condition. The question of whether a given bond is chemical or physical appears to the authors a futile controversy since, as with most rubber problems, both chemical and physical factors play their simultaneous parts.

For the early history of the bonding of rubber to metals, the reader is referred to the paper by B. J. Habgood[1].

1. TYPES OF BONDING AGENTS

1.1. Phenol-formaldehyde resins (PF).
1.2. Polyisocyanates (PI).
1.3. Cements based on chlorine derivatives of rubber (CDR).
1.4. Ebonite.

1.1 *PF cements*

(1.11) *For metal bonding.*—To obtain a good bond it is essential to use a rubber soluble resin and to give a very long cure. The development of accelerators for the curing of rubber with PF resins will undoubtedly result in the wider use of these cements. The bond is good, and fast to heat and solvents. PF resins are widely used for sticking rubber to metals, but the resin is not in such cases taken to the C stage and, hence, the bond is not of the same quality.

(1.12) *For textile bonding.*—The cement generally used for bonding rubber to rayon is a mixture of resorcinol-formaldehyde and latex[2]. It gives a good bond but suffers from the two defects of stiffening and staining the textile. Its advantage is it is used in water.

1.2 *PI cements*

(1.21) *For metal bonding.*—These cements can be used in straight organic solvents or, better, mixed with a solution of a synthetic rubber or chlorinated rubber to protect them against moisture formed by the too rapid evaporation of the organic solvent. On the whole, when tested by a discriminating method

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 25, No. 6., pages 378–406, April 1950.

(by impact), they give higher strengths than do other cements. The bonds are fast to heat and solvents and are better able to withstand continued fatigue. The polyisocyanates suffer from the disadvantage that they are highly reactive chemicals and must be treated as such by preventing them from coming into contact with mosture or the skin. For many uses the better results justify the extra care necessary in using them.

(1.21) *For textile bonding.*—Up to the present it has been necessary to use polyisocyanates in organic solvents. In spite of the fact that they gave higher bond strengths and no staining, their use was restricted by the fire and recovery losses associated with the use of organic solvents. Products (patent applied for) are now available which are stable to water and, in fact, can be used in aqueous suspension either alone or (where a green tack is required) in combination with latex. This represents a big advance in polyisocyanate bonding technique.

1.3 *CDR cements*

These cements are not easy to design. When used with Neoprenes, the cement can be a straight solution of chlorinated rubber[3], (B.P. 493,139) but for use with a wide latitude of natural rubber compounds, the preparation of the cement is far from easy. The position is in many ways analagous to the preparation of a PF molding powder: to prepare such a powder for one particular set of conditions is not difficult, but to make a powder with wide applicability calls for considerable knowledge and skill.

The preparation of a good CDR cement involves the use of two main ingredients: one to bond to the metal, the other to the rubber. If these two ingredients are simply mixed together in the resulting layer of bonding agent on the metal, the bond to either the metal or the rubber is only roughly one-half what it would have been if either agent, respectively, had been used alone. This difficulty can be largely overcome by arranging the mixture in such a way that the bonding agent for the metal settles out and concentrates itself on the surface of the metal. The top layer is now largely the agent for bonding on to the rubber. To prove this point the top layer can be removed by wiping with acetone or slight abrasion with sand paper, when it will be found that it no longer forms a good bond when vulcanized in contact with rubber.

CDR cements cannot be used for bonding to textiles.

1.4. *Ebonite*

The ebonite bond subjected to slow straight pull is extremely good, but its resistances to shear and shock are poor. Contraction of the ebonite would increase the bond when placed on the outside of a steel rim (the old use of ebonite for bonding solid tires to steel rims), but would lessen it in other circumstances.

2. COMPARISON OF THE EFFICIENCY OF BONDING AGENTS WITH DIFFERENT METALS

Throughout the present work a conventional tread stock, based on natural rubber with mercaptobenzthiazole as accelerator, was employed. This compound was bounded to aluminum, duralumin, mild steel, stainless steel, cast iron, monel metal, phosphorbronze, copper, and brass with a CDR cement[4], and with a polyisocyanate. The polyisocyanate was Vulcabond-TX. The test-pieces were the normal A.S.T.M. discs, and were tested on a Dennison machine at a speed of 1 inch per minute. The results obtained are given in Table 1.

TABLE 1

BOND STRENGTHS (lb. per sq. in.)

Metal	CDR cement	PI cement
Aluminum	800	785
Duralumin	875	635
Mild steel	785	835
Stainless steel	675	675
Cast iron	708	1185
Monel metal	500	445
Phosphorbronze	575	330
Copper	150	No bond
Brass	295	810

The results in Table 1 show that it is possible to obtain good technical bonds with both types of bonding agents to the following metals: mild steel, stainless steel, aluminum, duralumin, and cast iron. Poor bonds are obtained with copper and phosphorbronze. Although bonds were obtained with monel metal, we found that, on average, the bonds were weak and could be destroyed during removal from the mold. This applied to a lesser degree to stainless steel, but in this case the bond strength is higher and, therefore, the chance of removing the test-piece safely from the mold is greater. In other words, although we have obtained reasonable bond strengths with stainless steel, we suspect that if the process was introduced into a factory there would be a high proportion of rejections. For the same reasons it is very doubtful whether useful bonds could be obtained with monel metal by using either of these bonding agents in a factory.

Normally no bonding agent would be used with brass, but the results are given in Table 1 to complete the series.

Both bonding agents were used to bond the above natural-rubber tread stock to mild steel, and the bond strengths in shear and straight pull were determined.

TABLE 2

BOND STRENGTHS (lb. per sq. in.)

	CDR cement	PI cement
Mild steel		
Straight pull	785	835
Shear	905	930

It will be noted that the result obtained in shear is always greater than the result in a straight pull, a conclusion in accord with our general experience.

It is well known that it is more difficult to bond nitrile rubbers than natural rubber to metals. Using Vulcabond-TX, a bond strength of 995 lb. per sq. in. was obtained in straight pull when a tread stock based on Hycar was bonded to mild steel.

To complete the comparison of the CDR and PI cements, Table 3 gives the results obtained with these cements, using mild steel test-pieces (A.S.T.M. $\frac{1}{2}$ inch thick natural-rubber tread) when tested in straight pull, impact, and after fatigue.

TABLE 3

	Straight pull (lb. per sq. in.)	Impact strength (ft. lb.)	Strength after fatigue (per cent)
CDR cement	785	116	20
PI cement	835	220	90

The relation between the three methods is discussed later in the paper, and it is sufficient to note at this point that the PI cement gives a bond which is much more resistant to impact and fatigue than is the CDR cement.

3. APPLICATION OF BONDING AGENTS

3.1 *General considerations.*—The limiting factor in the design of a rubber-metal engineering unit is the strength of the rubber. It is important to distinguish between bond strength and unit strength. The limit of the unit strength in a perfectly designed and manufactured unit is the strength of the rubber which is contained in the unit. The bond strength in the unit can be considerably smaller than the strength of the unit, since the rubber is consuming energy in the process of deformation. This would, of course, not be true at extremely high rates of loading, but such rates are never likely to be met in practice.

The ideal design is to arrange for the normal small deformations to take place in shear but to take care of abnormal loads under compression, where the safety factor is considerably greater and the rubber acts as its own damper or stop.

With proper design, *i.e.*, sufficient rubber, the present bonding agents are more than capable of meeting requirements with an adequate safety factor.

3.2 *The design of the rubber compound.*—The quality of the rubber should be the highest obtainable to meet the required conditions.

(3.21) For rubber springs it should be dynamically soft (say about 40° Shore), and, if the frequency of loading is reasonably high, it should be of low hysteresis.

(3.22) it should have the highest tensile strength compatible with other requirements.

(3.23) it should possess good heat resistance.

(3.24) it must be free from grit, since a particle of grit is likely to start a fracture in the rubber.

(3.25) it must contain a minimum of substances which interfere with bond formation, for example, paraffin wax.

(3.26) it must be capable of working with the selected bonding agent from the point of view of composition or time of cure, or a tie-stock must be employed.

3.3 *Curing of the rubber in the unit.*—This must be done with minimum washing off of the bonding agent from the treated metal surfaces. This should not be confused with the minimum movement of the bulk of the rubber in the mold, but with surface movements of the rubber. Injection molding under certain conditions and transfer-molding in general give excellent bonds, since the surface movements are negligible due to first contacts creating the bond[15]. Stripping tests often reveal different strengths in different directions, and one cause of this is the superimposed stress at the bond due to calender grain. Calender grain is avoided by any of the injection methods of molding.

Care should of course be taken not to employ a faster curing compound than that required by the particular cement to create a good bond.

Annealing or slow cooling is sometimes desirable where the rubber has a superimposed stress, *e.g.*, bonds with rubbers which give high shrinkages.

3.4 *Some causes of failure*

(3.41) *Breaks in the rubber*

(3.411) poor or unsuitable quality.
(3.412) presence of grit.
(3.413) delamination.
(3.414) bad design of the unit such as too big load, allowing the distortion to pass through neutral point, etc.

(3.42) *Breaks in the bond*

The bond may be:

(3.421) that between the metal and the bonding agent;
(3.422) that between the bonding agent and the tie-stock (when used); or
(3.423) that between the tie-stock and the rubber.

Assuming that a satisfactory bonding agent has been used, the breaks under (3.421) are probably due to bad cleaning of the metal or unsatisfactory application, *e.g.*, too much or too little or insufficient drying or too much brushing, of the bonding agent.

Breaks under (3.422) and (3.423) are usually the result of using an unsuitable tie-stock. A slight increase in the sulfur in the tie-stock often puts this defect right.

Lastly, breaks under (3.421), (3.422) and (3.423) may result from other causes, such as a local excessive peak load arising from a too sudden change of properties from a rigid bond to a soft rubber or contraction of the rubber, *e.g.*, acrylonitrile rubbers, or bad design. Good design removes the point of initial deflection some way from the bond (by making the area of the bond greater than the area of the rubber at the point of flexion), and always ensures sufficient rubber to reduce the peak load developed at the bond far below its safety value.

4. THE TESTING OF BONDING AGENTS AND BONDING UNITS

(4.1) *The testing of textile bonding agents*

It has been recognized by many authors that the normal stripping test involving a measurement of the average load to peel a 1-inch strip of fabric at the rate of 10 cm. per minute is not sensitive enough to discriminate adequately between different types of bonding agent. An interesting point is raised in a recent paper[6], where it is pointed out that a high stripping load (associated with a high deposit on individual cords) does not necessarily mean better performance in service.

During the war Roelig[7] designed a cord adhesion test for tire cords, where 24 cords were spaced at $\frac{1}{8}$-inch intervals in a rubber strip of the following dimensions: $15 \times \frac{3}{4} \times \frac{1}{4}$ in. The rubber is held in a slotted holder; each cord is attached to a 1-kg. weight, and the sample holder oscillates through 1.9 mm. at a speed of 250 cycles per minute. The bond between the cord and the rubber is, therefore, fatigued.

A similar type of machine was designed independently in this country by Pittman and Thornley[8], and in this case they fatigued the cord by compressing the rubber rod containing the cord. In both cases fatigue can be measured either by noting the number of cycles to produce complete breakdown when the cord will pull through by hand, or by measuring the force required to pull through single cords after definite time intervals.

Shape factor in its broadest sense may play a part in the testing of tire cord-rubber bonds. In the Roelig and Henley machines, the individual cords are surrounded with a mass of soft carcass stock rubber which distorts easily. This distortion may play some abnormal part in both the fatiguing and the ultimate testing of the bond. In the tire, however, the surrounding rubber is stiffened by the presence of other cords, which are spaced at approximately 24–26 to the inch. To test the importance of this factor, the Roelig machine was modified so that a test piece with 24 cords per inch could be used.

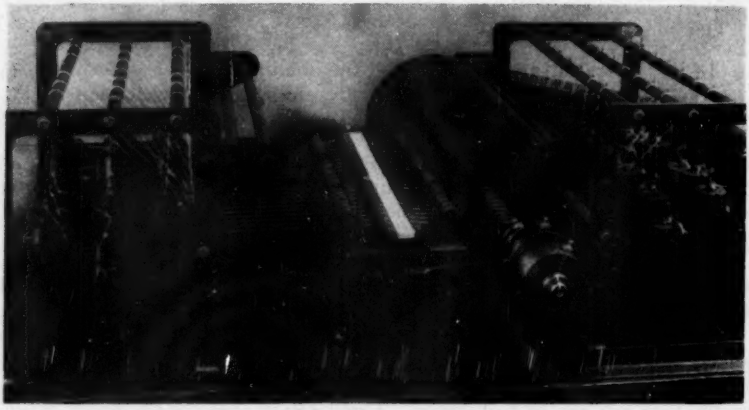


FIG. 1.

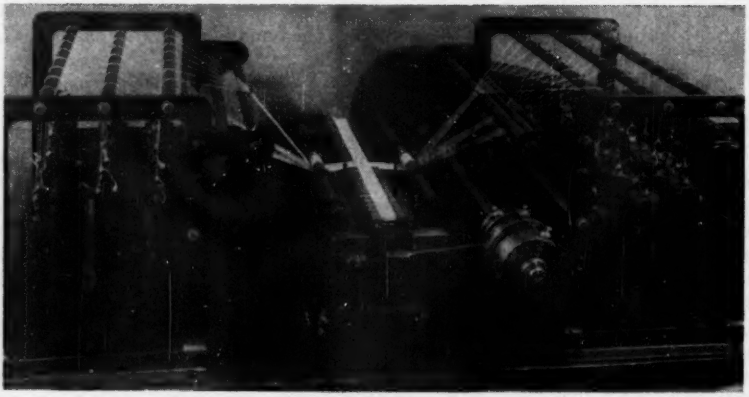


FIG. 2.

The normal Roelig apparatus is shown in Figure 1 and the I.C.I. modified apparatus in Figure 2. In the Roelig apparatus, the 24 cords pass through slits in a guide bar and then pass over rods to the tensioning weights. The weights are in three sets of eight, one set under each rod.

In the modified apparatus three additional guide bars have been fitted to each side of the apparatus and eight cylindrical pegs fitted to each bar in the form of a comb. The 24 cords are divided into three sets of eight by the three

combs, and are then led over the bars to the tensioning weights. To ensure that the correct spacing of the cords is obtained, the bars above the tensioning weights have been fitted with eight cylindrical stops, one above each weight. The sample holder has been modified; the central inch is cut away so that the lower $\frac{1}{32}$ inch of the rubber is firmly clamped. Two strips of metal 1 inch long and $\frac{1}{32}$ inch deep, $\frac{3}{4}$ inch apart have been screwed to the under face of the top clamp, which carries the electric heaters. When the sample is finally in position, therefore, there is $\frac{1}{16}$ inch gap in the center, through which the cords are led away, and the rubber above and below the cords is held firmly in position. If this were not done, no fatigue would occur at the bond between the cord and the rubber. In our apparatus the sample holder oscillates through 1.75 mm. at a speed of 375 r.p.m.

The modified apparatus can, therefore, be used to carry out either test. It was desirable that the mold should be such that both types of test-piece could be prepared in it. This mold is shown in Figure 3 and meets this requirement.

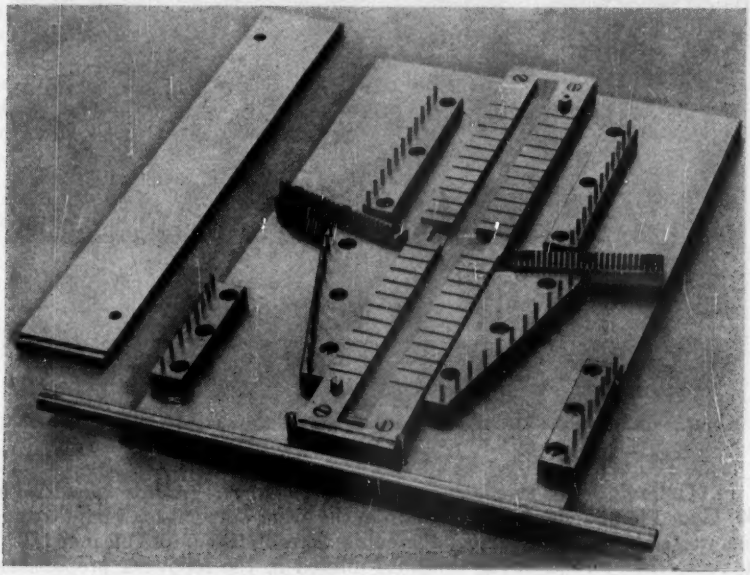


FIG. 3.

It will be seen that the central inch is cut away in two stages. The difficulty was to prevent the rubber extruding along the cords when there was a gap 1 inch wide. The problem was solved by fitting a piece of cured rubber in the recessed portion. Figure 4 shows the mold with the bottom strip of rubber in position. The cords are then put in position as illustrated, and another piece of cured rubber is placed on top of the cords above the recess. Metal stops are then dropped into position alongside this piece of rubber. The top half of the rubber to which the cords are to be bonded is then placed in position and the mold is closed. This method is effective in sealing the mold so that no extrusion occurs along the cords. After removal from the mold, the cured rubber inserts are easily removed from the cords. During cure each end of a cord is attached to a tensioning weight of 2 pounds.

In our experience polyisocyanates generally give higher initial bonds than does the latex-resorcinol-formaldehyde agent when measured either by a stripping or peeling test or by measuring the load to pull out single cords from the rubber. It is also our experience that the rate of decrease in bond strength due to fatigue is approximately the same in the two cases and, therefore, the higher initial bond strength of the polyisocyanate is an advantage shown throughout the life of the bond.

The methods we used to prepare the test-pieces are given below.

The cords consisted of rayon 3-ply tire cord cut to lengths or approximately 4 feet.

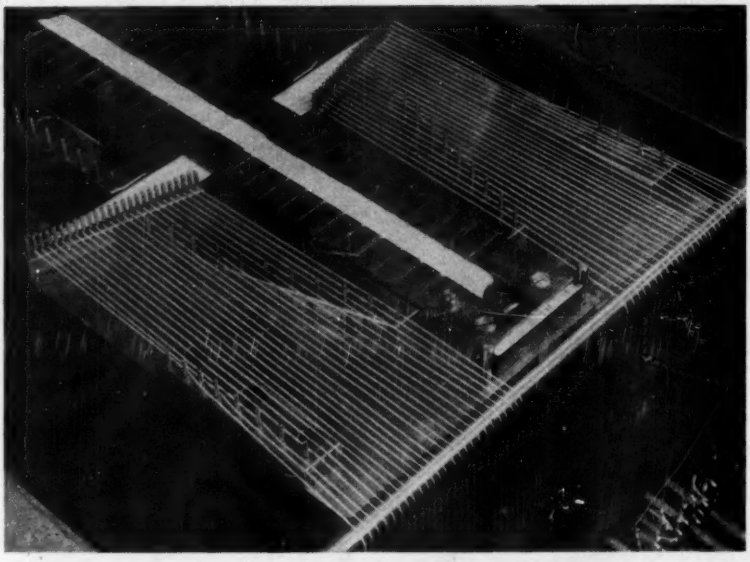


FIG. 4.

(4.11) *Cords treated with latex-resorcinol-formaldehyde.*—Cords were dried at 100° C for 1 hour and, after removal from the oven, were left for 5 minutes and then weighed. After weighing, the cords were dipped into Vulcabond-T (a latex-resorcinol-formaldehyde solution) diluted in the following proportions: bonding agent, 1 part, water, 2 parts. The dipped cords were then squeezed between glass rods and hung to dry. After drying overnight the dipped cords were baked in the oven for 30 minutes at 100° C. Five minutes after removal the cords were reweighed, and the amount of latex-resorcinol-formaldehyde deposited was calculated.

(4.12) *Cords treated with PI cement (Vulcabond-TX).*—A 3 per cent rubber solution of a standard carcass compound was used, and 50 per cent Vulcabond-TX on the weight of rubber was added. The cords were dried in the oven for 1 hour at 100° C before dipping. The procedure was then the same as for the latex-resorcinol-formaldehyde.

(4.13) *Treatment with aqueous dispersion of PI cement.*—The procedure corresponded to that used with latex-resorcinol-formaldehyde.

The results obtained after fatiguing for 4 days at 80° C are given in Table 4.

TABLE 4

Bonding agent	Number of cords	Load to pull out a single cord (lbs.)	
		Not fatigued (lb.)	After 4 days at 80° C (lb.)
Latex-resorcinol-formaldehyde (Vulcabond-T)	Single $\frac{1}{4}$ inch apart,	8.2	6.9
	24 cords per inch	11.3	9.6
PI cement (Vulcabond-TX)	Single $\frac{1}{4}$ inch apart,	9.8	8.8
	24 cords per inch	12.5	11.0
Water dispersed PI cement	Single $\frac{1}{4}$ inch apart,	8.1	7.1
	24 cords per inch	10.4	9.2

The results in Table 4 show that, with the 24 cords to the inch test-piece, the structure is stiffer and the load to pull out a single cord is greater than that required for single cords spaced $\frac{1}{4}$ inch apart. The results after fatigue indicate that, as expected, the looser structure (with cords $\frac{1}{4}$ inch apart) protect the bond during fatigue in this test because conditions of constant amplitude are used. The three bonding agents tested here are placed in the same order by the two tests, but a different order might be obtained with other bonding agents. In our opinion the test using 24 cords to the inch is to be preferred, since it approximates more closely to service conditions.

For the testing of bonding agents used in the proofing industry, we prefer the du Pont scrub test.

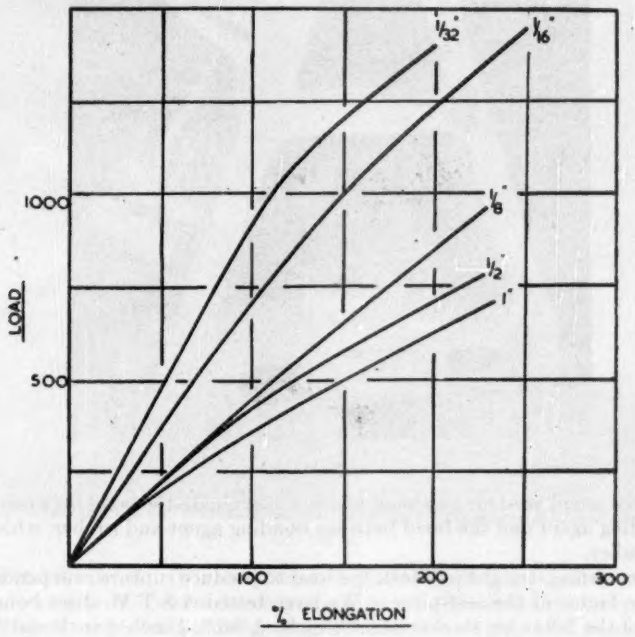


FIG. 5.

4.2 *The testing of metal-bonding agents*

It is widely recognized that present methods of evaluating rubber-to-metal bond strengths are completely inadequate. In the normal test[9] the break often occurs in the rubber, and the test-piece is not subjected to uniform stressing. Due to necking of the rubber the stresses are a combination of straight pull and shear. The present authors cannot think of any application in practice where the A.S.T.M. test conditions are simulated.

In service early failures are often due to shock and practically never due to slow loading. The A.S.T.M.[9] recognize the inadequacy of the standard test, and the fact that they specify five different types of failure shows that, at these slow rates, it is impossible to guarantee that it is the bond which is being tested.

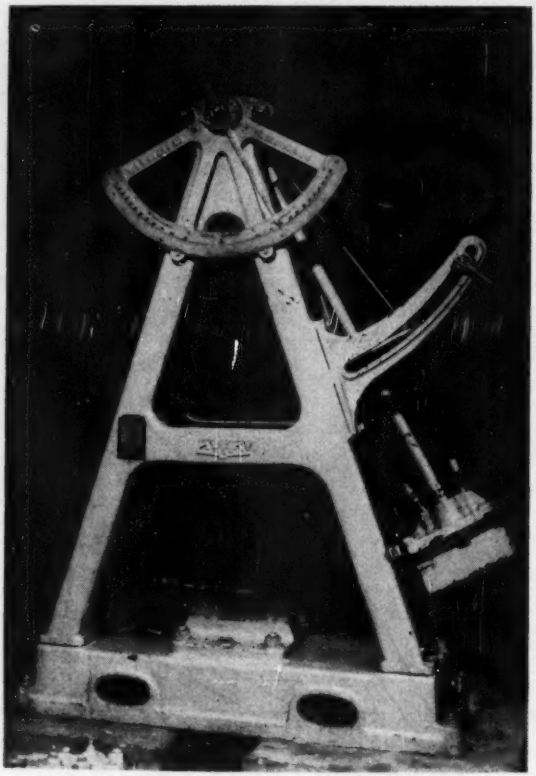


FIG. 6.

There is a real need for a method which will evaluate the bond between metal and bonding agent and the bond between bonding agent and rubber, whichever is the weaker.

In the normal straight pull test, the load to produce rupture is dependent on the shape factor of the test-piece. We have tested A.S.T.M. discs bonded to rubbers of the following thicknesses: $\frac{1}{32}$ inch, $\frac{1}{16}$ inch, $\frac{1}{8}$ inch, $\frac{1}{2}$ inch and 1 inch, and have found that, even with the $\frac{1}{32}$ inch thick test-piece, some necking of the

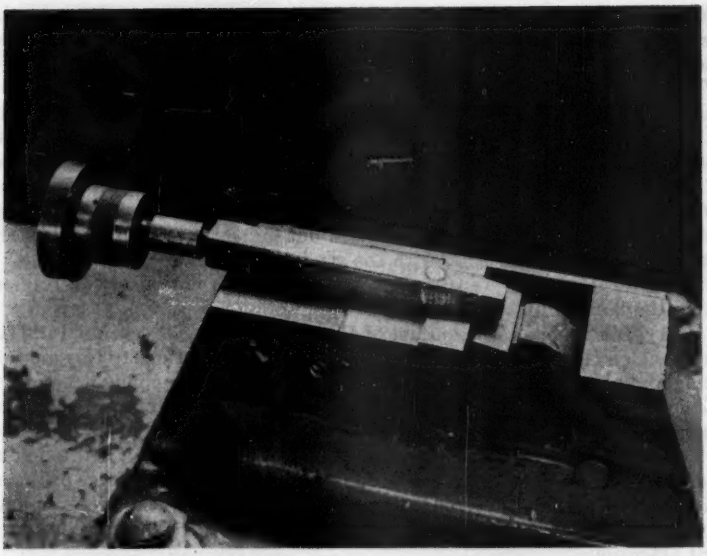


FIG. 7.

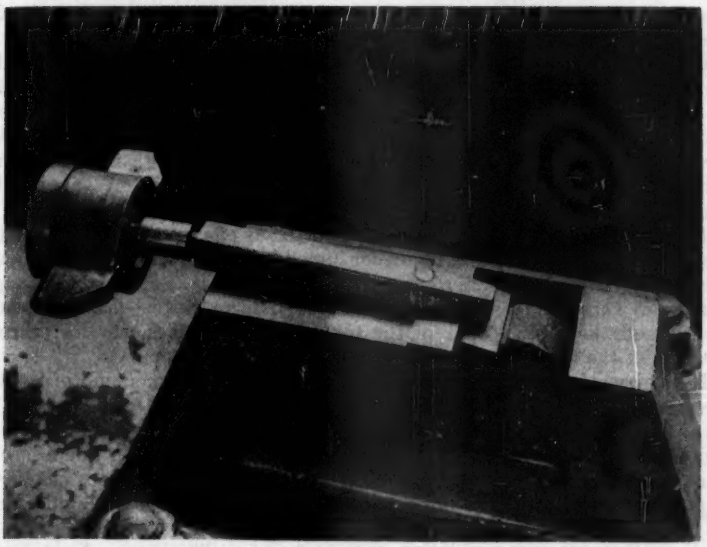


FIG. 8.

rubber still occurred. The more the test-piece deforms, the more it necks, and a shear component of stress develops near the junction of the rubber and metal. This difficulty is met when different thicknesses are used or with compounds of different hardnesses which deform to different extents. The graph shown in

Figure 5 gives the stress strain curves for the above units of different thicknesses, and it will be seen that as the thickness of the rubber is reduced so the stress strain curve is raised, *i.e.*, the unit is stiffer.

The whole stress system in this type of test-piece is complicated, and it is doubtful whether any comparison of bonded units with different compounds can be justified because of the variable stress systems imposed on the test-piece. Tests in shear are much sounder, although Rivlin[10] has shown that the shear is not a pure shear on account of the presence of stresses perpendicular to the planes normal to the shear planes. Shear tests are still subject to the influence of shape factor[11], but experiments carried out indicate that the effect of shape factor is less pronounced than with the straight pull tests.

In our experiments, we have decreased the deformation of the rubber by testing the bonded unit by impact.

(4.21) *The Izod machine.*—First of all we modified a conventional 120 ft.-lb. Izod machine (Figures 6, 7 and 8), but as there are objections to this method of testing and also because the machine did not have a high enough capacity, we designed a falling-weight machine (Figures 9 and 10), where both the velocity of impact and the available energy of impact could be varied over a wide range.

The field of impact testing is one of the most controversial, and much more fundamental work is required with a range of materials before some of the more difficult problems can be solved. It is outside the scope of the present paper to discuss all the limitations of impact testing, but there are several points which merit attention.

In the Izod test (Figure 6) the test-piece is broken by a single blow of a heavy calibrated pendulum. The energy absorbed in the fracture of the test-piece is determined by the calculation of the energy of blow indicated by the initial position of the pendulum and the remainder indicated by the highest position on the opposite side which is reached by the pendulum after breaking the test-piece. The pendulum type of test with metals and plastics possesses two fundamental disadvantages, namely, the results must be obtained on test-pieces of standard dimensions and cannot be compared with results obtained with test-pieces of other dimensions, and the results do not measure the true energy required to fracture the test-piece.

It has been shown[12] that the value reported as energy to break of the test-piece is really the sum of the energies consumed by several different mechanisms, such as the energy to initiate fracture of the test-piece, the energy to propagate the fracture across the test-piece, the energy to deform the test-piece, the energy to throw off the broken ends of the test-piece, and the energy lost through vibration of the apparatus and its base, and through friction.

It has been found that the energy absorbed by the broken end of the test-piece may represent a large fraction of the total energy used in the test[13]. The arrangement of the test-piece in our experiments is shown in Figures 7 and 8. Figure 7 shows how the test-piece is fitted in the sample holder and a circular metal disc is screwed to one end of the test-piece. A metal plate is fastened to the striking hammer, and, a uniform blow is transmitted to the circular metal disc by the circular collar shown in Figure 8. These accessory parts also absorb energy, and therefore in our tests more energy is used to throw off the broken end of the test-piece along with the accessory parts than in the normal metal test.

The energy absorbed by different test-pieces varies greatly from one to the other, so the excess energy left in the pendulum is unpredictable. This is regarded as a serious disadvantage of the pendulum method of impact testing.

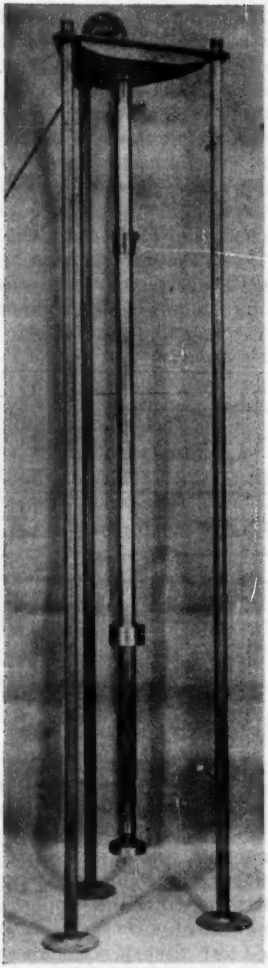


FIG. 9.

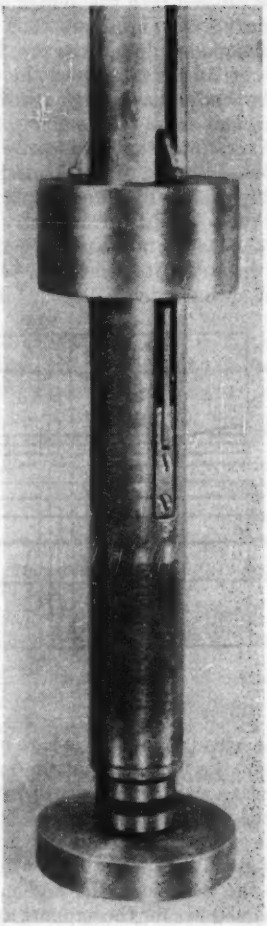


FIG. 10.

It is not known what effect the presence of an excess of energy would have on the result obtained with a bonded test-piece, but it seems wisest to be guided by the experience gained with metals and insulating materials.

(4.22) *The falling-weight machine.*—The falling-weight machine (Figure 9) was therefore constructed. The test-piece is screwed into the bottom of the central column, and a circular metal disc is screwed on to the under side of the test-piece (Figure 10). An adjustable collar can be moved to any position on the central column, and can be clamped at any desired height. The weight is pulled up by a rope which passes down the inside of the hollow central column. The rope is attached to the three parts of the weight support, and as the weight

is raised to the level of the clamped cylinder, the projections of the weight support are pushed into the center of the hollow column. Only two of the projections are shown in Figure 10. As the top of the weight reaches the bottom of the clamped cylinder, the projections are pressed back sufficiently to release the weight, and it falls down the tube on to the test-piece.

In Appendix I, a mathematical solution for the simple case of a falling weight is given, and some of the general conclusions are summarized here. For example, it is shown that a suddenly applied load produces a much greater tension than that due to a static loading of equal magnitude. By representing our bonded test-piece by a metal spring, it has been shown that the stress is diminished if the rubber deforms to any great extent. As the static elongation under a constant load is increased, the effect of impact is decreased. In the case discussed the stress at impact can be diminished by a factor of slightly more than 14 if the spring extends 1 inch. This emphasizes how important it is to ensure

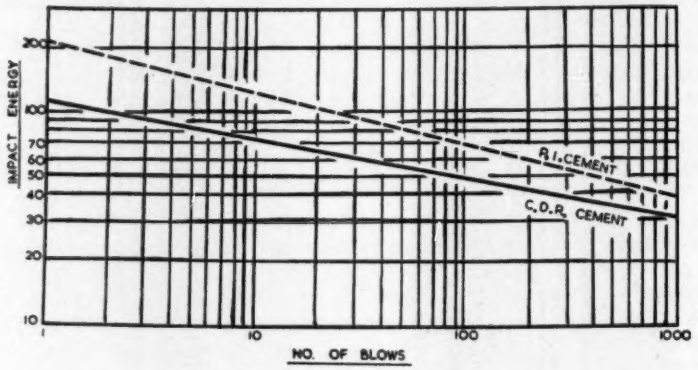


FIG. 11.

that the speed of testing is high enough so that the rubber component does not damp out the formation of the maximum stress. The alternate method is to work with a very thin layer of rubber.

In the construction of the falling-weight machine, it is important to ensure that the supports are rigid and free from vibration. A slightly different treatment is given in Appendix II, which proves that the stiffer the support in relation to the test-piece, the higher is the ultimate load. By choosing suitable spring constants for the support and the bonded test-piece, it is calculated that, in our experiments, only 2 per cent of the maximum load is not developed.

With the falling-weight machine, there are three possible methods of carrying out the test.

(4.221) *The Probit method.*—First there is the Probit method[14], which consists of preparing (say) 30 test-pieces and dividing these into sets of five. All the test-pieces in a set are subjected to blows from the same energy level, and a different energy level is used for each set of test-pieces. The percentage of breaks in each set is plotted against the energy of blow applied to that set, and a smooth curve is drawn on which the blow which would have broken 50 per cent of the test-pieces is interpolated. This blow is taken as the impact strength of the material.

The values chosen for the energy level applied to the different sets of test-pieces are such that at least one point of the curve lies below 50 per cent and

above 10 per cent fractures, and at least one point lies above 50 per cent and below 90 per cent fractures. This method appears to give the information which is of interest to the designer, namely, the maximum blow which a test-piece can withstand without rupture. The method can be criticized on the grounds that a large number of test-pieces are required and that information on the energy required to break individual test-pieces is not obtained. This criticism is not very serious, however, if the method gives useful results.

(4.222) *The multiple impact method.*—The second method which we have used is a multiple impact method. Various weights were dropped from different heights, and the number of impacts required to produce the first signs of breakdown and the complete rupture were noted. By extrapolation from these results, it is possible to estimate the energy required just to produce rupture with a single blow (Figure 11). With this method the effects of fatigue may give slightly low results.

(4.223) *The repeated blow method.*—The repeated blow method[15] used by Church and Daynes on ebonite has been investigated. In this method the test-piece is struck with an energy slightly below that required to fracture and then applying to the same test-piece blows increasing by increments of about 10 per cent until fracture occurs. With bonded test units however it appears that fatigue is always sufficient to lower the result.

The results obtained by the three methods with two bonding agents, using A.S.T.M. test-pieces (natural-rubber tread—mild steel) are summarized in Table 5.

TABLE 5

	Probit method (ft.-lb.)	Multiple blow (ft.-lb.)	Repeated blow (ft.-lb.)
CDR cement	125	116	105
PI cement	220	220	170

These results show conclusively that the PI cement bond is intrinsically much more resistent to shock-loading than the CDR cement bond. Good agreement is obtained with the Probit and multiple blow methods, but to remove the effects of fatigue, the Probit method is preferred. The repeated blow method is particularly sensitive to fatigue and should only be used as a rough sorting test when there are not sufficient test-pieces to use the Probit method. It is better to measure fatigue more directly by the methods which will now be described.

(4.23) *Fatigue of bonded units*

Most bonded units are subjected to repeated stressing in service, and therefore it is important to test the unit after various cycles of loading. Fatigue occurs not only in the bond itself but also in the rubber.

(4.231) *The Goodrich flexometer.*—The test-piece holder on the Goodrich flexometer was modified so that the normal A.S.T.M. bonded test-piece could be accommodated. The test-piece was submitted to extension, but was not subjected to compression, *i.e.*, the mass of the rubber did not pass through its zero position. In these circumstances most of the fatigue occurs in the region of the bonding agent, where the deformation of the rubber is restricted.

Both the PI cements and the CDR cement bonding agents have been tested under various strokes of 0.1, 0.15, 0.20, 0.25, and 0.30 inch. As an example, using a stroke of 0.20 inch in the Goodrich flexometer, *i.e.*, a deflection of 40 per cent on the rubber thickness, the unit with CDR cement lost 80 per cent of

its strength after 2 hours' fatiguing, whereas under the same conditions the unit with PI cement lost only 10 per cent of its strength. Under these conditions, therefore, the PI cement is superior to the CDR cement type of bonding agent. Indeed, the newer methods we have developed, *e.g.*, both impact and fatigue, discriminate clearly between the two bonding agents, whereas the conventional straight pull method does not discriminate at all. The defects of the straight pull method have been realized for a long time, but it is doubtful whether the extent of the uselessness of straight-pull tests was fully realized until the present results were obtained. The results obtained by the three methods have been summarized in Table 3.

(4.232) *Falling weight fatigue method.*—Fatigue tests can be carried out by the falling-weight method. The 20-pound weight was dropped from a height of 3 ft. and the percentage drop in strength was measured on the Dennison after various multiple blows with the 20-pound weight. The results from the 0.1 inch stroke on the Goodrich flexometer and the impact method are plotted in Figure 12. The shape of the curves is quite different because each blow on the

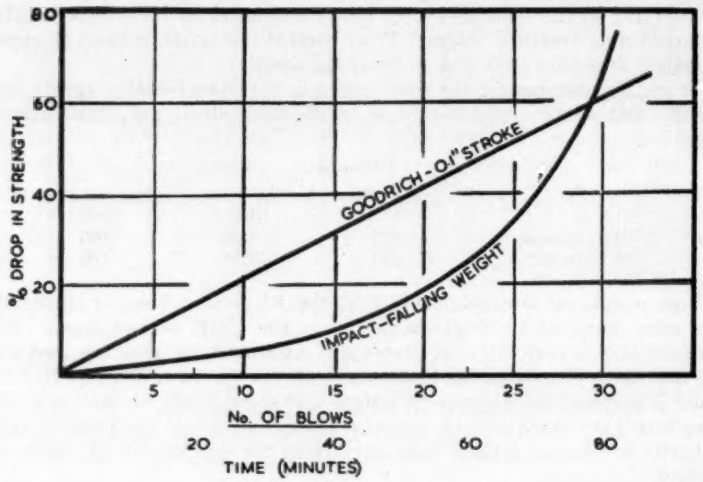


FIG. 12.

impact method has a relatively high energy level and therefore the rate of drop increases more rapidly as the test continues. With the Goodrich method, the energy input tends to be more continuous at a much lower level. It appears from the results in Figure 12 that a 60 per cent drop in bond strength is produced by 29 impacts (total energy input 1740 ft.-lb.), whereas 80 minutes with the stroke of 0.1 inch on the Goodrich flexometer means that the energy input has been approximately 25,000 ft.-lb. This apparent discrepancy in the energy levels is resolved if we refer to Figure 11, where it is shown that as the logarithm of the energy level is decreased, the logarithm of the number of blows (and hence the total energy input) increases.

Although certain applications may demand an investigation of the effect of varying the stroke, there is much to be said for keeping the stroke low (in the region of 10–15 per cent of the thickness of rubber) in any routine comparison of bonded units. Both methods of fatiguing the unit give useful information to

the design engineer. The type of fracture obtained after fatigue is of interest. Normally after fatiguing in the Goodrich flexometer, where in our tests the deformation is purely an extention, the fracture occurs in the rubber in the region close to the metal. Fatigue is greatest in the region of greatest restraint, *i.e.*, in the region of the bond. The type of fracture obtained is essentially brittle and is characteristic of fatigue. A range of test-pieces fatigues for various times are illustrated in Figure 13, and they show how the fatigue failure starts

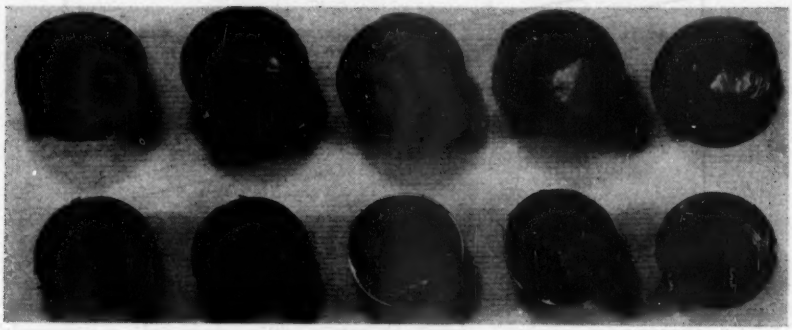


FIG. 13.

at an edge and spreads inward to the center of the test-piece at the same time that it spreads round the circumference of the test-piece. The piece of rubber with the smooth broken surface indicates a plastic fracture, and is the portion of rubber which is ruptured during the test either by straight pull or by impact. This phenomenon is similar to the type of fractures obtained with metals after fatigue. These results indicate that PI cements not only give a stronger bond, but produce, possibly by a gradation of physical properties from the immovable rubber in contact with the metal to the soft mass of the rubber, a condition in the rubber capable of withstanding greater fatigue.

5. EFFECTS OF SHAPE AND STIFFNESS

5.1 *Effect of shape factor*

Earlier in this paper the authors have referred to the difficulties introduced into testing by the shape factor of the test-piece. To check the influence of shape factor on impact, strength tests were carried out by the multiple blow method. The results obtained with A.S.T.M. test-pieces having $\frac{1}{16}$, $\frac{1}{8}$, $\frac{1}{4}$, $\frac{1}{2}$ and 1 inch thickness of natural rubber tread bonded to mild steel are summarized in Figure 14. It will be seen that the impact strength is decreased from 220 to 76 ft.-lb. as the thickness of the rubber is reduced from 1 to $\frac{1}{16}$ inch. This is due to the fact that as the rubber deforms and the peak stress developed under impact is reduced. In the theoretical case considered in Appendix I, it is shown that if a metal spring extends 1 inch, the stress at impact can be diminished by a factor of slightly more than 14.

To check the validity of this view, the peak stresses developed during impact were measured. It is not proposed to describe in the present paper the methods used in any detail, and it is sufficient to say that 4 strain gauges were mounted on a metal cylinder, which was placed just above the top of the test-piece. These gauges formed the four arms of a Wheatstone bridge circuit, and

the out of balance voltage was amplified by means of a d.c. amplifier, and the response on a cathode ray oscillograph was photographed. The strain gauges were calibrated statically, and with this equipment magnifications of the order of 3000 were possible.

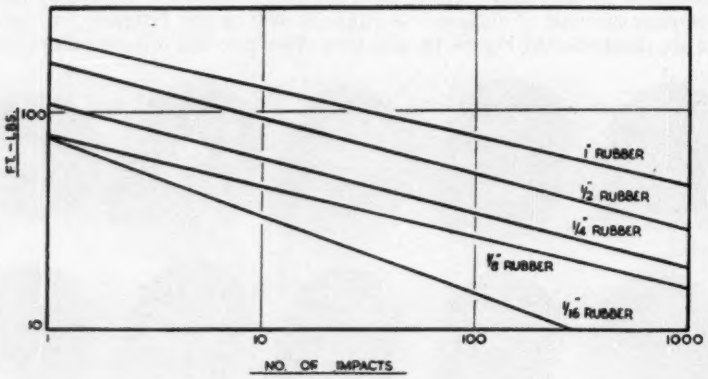


FIG. 14.

In our experiments a 20-pound weight was dropped from a height of 2 ft. 9 in. (energy input 55 ft.-lb.), and the results obtained are summarized in Table 6.

TABLE 6

PEAK LOADS DEVELOPED UNDER IMPACT

Thickness of test-piece (in.)	Peak load (lb.)
1	630
½	960
¼	1380
⅛	1660
1/16	2110

In Appendix III the effect of the length of the test-piece is considered in relation to the breaking stress, and it is calculated that, for a given energy input, stress is inversely proportional to the square root of the length of the test-piece. It will be seen that the above measured peak loads approximate to this rule. This agreement with theory can be considered as satisfactory in view of the assumptions made in Appendix III, and also because the above loads are the peak loads after transmission through the rubber test-piece. Measurements of the peak loads on the striker plate before transmission through the rubber test-piece are in hand. From these two measurements, we can obtain useful information on the effect of the damping action of the rubber on the peak stresses developed.

The implications from Appendix III are that the only important factors governing either the energy of rupture or the breaking stress are the volume of the rubber test-piece and the modulus of the rubber stock. This subject will be dealt with fully in another paper when our further experiments are complete.

Meantime the authors have used a purely empirical method of correcting the impact strength to eliminate the effect of shape factor.

The peak loads for different thicknesses of rubber of cylindrical cross-section of 2 sq. in. area were measured by the electrical strain guage method when the energy input was 55 ft.-lb. It these loads are converted into percentages of the peak load developed with no thickness of rubber (or for practical purposes $\frac{1}{16}$ inch of rubber), the corrected bond strengths for these different thicknesses of

TABLE 7

Thickness of test-piece	Impact strength (ft.-lb.)	Peak load for an energy input of 55 ft.-lb.	Corrected impact strength (ft.-lb.)
1 in.	220	630 lb. = 30%	$220 \times \frac{30}{100} = 66$
$\frac{1}{2}$ in.	165	960 lb. = 45.5%	$165 \times \frac{45.5}{100} = 75$
$\frac{1}{4}$ in.	110	1380 lb. = 65%	$110 \times \frac{65}{100} = 72$
$\frac{1}{8}$ in.	78	1660 lb. = 79%	$78 \times \frac{79}{100} = 62$
$\frac{1}{16}$ in.	76	2110 lb. = 100%	$76 \times \frac{100}{100} = 76$

test-pieces can be obtained by calculating the appropriate percentages of the values obtained for the apparent bond strengths by any of the impact methods described in this paper. The corrected impact strengths are remarkably constant (range 62–76 ft.-lb.), and the standard error of these results is only 5.4. This empirical method of correction is useful if only because it emphasizes that, to obtain comparable results when comparing test-pieces of different thicknesses, the energy input should be increased as the thickness of rubber is increased so that the same peak stress is developed in the test-piece.

From our measurements of the peak loads we have also estimated the times of impact. The time of impact in the case of the $\frac{1}{16}$-in. test-piece was 7 milliseconds, and the time of impact is increased to 25 milliseconds in the case of the 1-inch test-piece.

5.2. *Effect of stiffness of the rubber compound*

To study the effect of the stiffness of the rubber compound on the peak loads developed under impact, a range of nine compounds containing different proportions of carbon black was studied. The test-pieces were the conventional A.S.T.M. mild steel discs with $\frac{1}{2}$ inch thick natural rubber, and the bonding agent was CDR cement.

The results obtained are summarized in Table 8.

TABLE 8

Compound	Tensile strength (kg. per sq. cm.)	Elongation at break (per cent)	Modulus (100%)	B.S. degrees	Bond strength (static) (lb. per sq. in.)	Impact strength	Peak load (lb.)
Gum	167	747	6	39	400	—	430
MPC Black 20	170	657	8	49	770	156	630
MPC Black 30	195	582	14	60	935	151	740
MPC Black 40	196	518	19	68	935	148	1050
MPC Black 50	195	452	24	71	950	134	1270
SRF Black 20	200	687	7	46	755	105	not tested
SRF Black 40	207	573	16	57	590*	86*	1050
SRF Black 80	163	385	36	69	1020	88	1380
SRF Black 100	131	225	68	83	975	84	1510

* Results appear to be low.

It is seen that, as the stiffness increases, the peak load increases, which agrees with our hypothesis and agrees with the previous results quoted for rubbers of different thicknesses. The test-pieces made from the SRF black compounds have the lower impact strength, but this is probably due to the fact that higher peak loads are developed with these particular compounds. It may not necessarily mean that MPC is intrinsically a better black for bonding than the SRF black.

6. SUMMARY

It is essential to distinguish clearly between the testing of bonds and the testing of bonded units.

6.1. *In testing metal bonding agents* (as distinct from bonds)

(6.11) The conventional straight-pull test is of little value, and should only be used as a rough sorting test to establish whether any bonding has taken place. In other words it only discriminates between a good and a bad bonding agent, but does not make possible a proper assessment when a range of good bonding agents is being evaluated.

(6.12) To evaluate bonding agents, the effects of impact and fatigue should be invesitaged, and the methods we have described appear to be suitable and worthy of study by other laboratories.

(6.13) In all cases where the problem is the evaluation of the bonding agent, the thickness of the rubber should be kept to an aboslute minimum, and we recommend a maximum thickness of $\frac{1}{8}$ inch.

(6.14) Although a full evaluation of the effects of fatigue would involve the study of different strokes on the Goodrich flexometer, we recommend, for routine tests, a stroke of 10–15 per cent of the thickness of the rubber.

(6.15) Where the investigation of fatigue under large energy inputs is important, the falling-weight method should be used.

6.2 *In testing bonded units*

The problem of testing complete bonded units is quite different and separate from the testing of bonding agents. The first essential is to know at least approximately the conditions to be met in service, *e.g.*, the amplitude and frequency of stressing, shock loads, the range of ambient temperatures, and the range of solvents, oils and vapors which the unit will contact, and the test should be carried out under these conditions. The absorption of energy by the rubber reduces the maximum shock on the bond, hence the unit is protected by using as soft and as thick a rubber as the limits of strength, stability, and space permit.

The difference between the two types of testing may be summarized by saying that, when testing metal bonding agents, one must ensure that the maximum loads or stresses are developed and imposed on the bond, whereas the design of a good bonded unit involves the protection of the bond against such stresses by utilizing the deformation and damping characteristics of the rubber. Testing of the effect of the bonding agent on the quality of the rubber in the immediate neighborhood of the bond by fatigue methods is also desirable.

6.3. *In testing cord bonding agents*

In the testing of bonding agents for tire cords, we prefer a fatigue test, with the normal number of tire cords per inch so as to reduce the factor of excessive distortion.

ACKNOWLEDGMENT

The authors wish to acknowledge the able assistance of V. Bryan, B. J. Habgood, T. J. Meyrick, I. F. Smith, R. L. Stafford, and G. E. Williams.

APPENDIX I

In the case of the falling-weight method, a mathematical solution has been worked out by Timoshenko[16].

Assume that a weight W (Figure 15) falls through a height h on to a stop mn in such a manner as to produce a simple tension in a bar of length l. Let $\lambda_{st} = Wl/EA$ represent the static extension of the bar under the action of the weight W and λ the extension produced under impact so that the complete vertical displacement of the weight W at the moment its velocity becomes zero is equal to $h + \lambda$; then the work done by this load during falling becomes $W(h + \lambda)$.

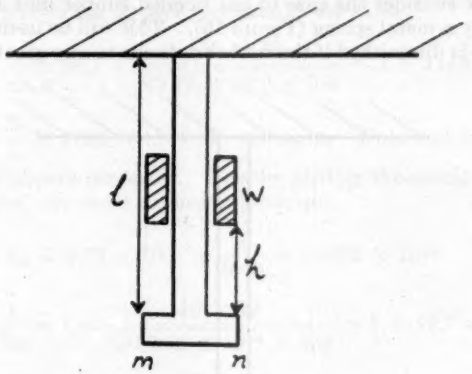


FIG. 15.

If the mass of the bar is small in comparison to the mass fo the falling weight, the loss of energy during impact is negligible, and it can be assumed with a sufficient accuracy that the work done during impact is completely transformed into the potential energy of the bar extension, provided the material has not exceeded its elastic limit. The expression for this energy is

$$U = \frac{\lambda^2 EA}{2l}$$

and

$$\frac{\lambda^2 EA}{2l} = W(h + \lambda)$$

$$\lambda = \lambda_{st} + \sqrt{\lambda^2_{st} + 2\lambda_{st}h}$$

If $h = 0$, $\lambda = 2\lambda_{st}$, and this means that a load suddenly applied produces twice as great an extension as that due to a static loading of equal magnitude.

In our case, where we are concerned with highly elastic systems, we prefer to think in terms of the tension produced and say that a load suddenly applied produces twice as great a tension as that due to a static loading of equal magnitude.

If h is large in comparison with λ_{st}:

$$\lambda = \sqrt{2\lambda_{st}h}$$

and the maximum tensile stress in such a case is:

$$p_{max} = \frac{E\lambda}{l} = E\sqrt{\frac{2\lambda_{st}h}{l^2}}$$

$$V = \sqrt{2gh} \text{ or } h = \frac{V^2}{2g}$$

$$p_{max} = E\sqrt{\frac{\lambda_{st}V^2}{gl^2}} = \sqrt{\frac{E}{Al}\cdot\frac{WV^2}{g}}$$

This means that the stress produced on impact depends, not on the cross-sectional area, but on the volume Al of the bar and on the kinetic energy of the falling weight.

Let us now consider the case of our bonded rubber unit and represent the bonded unit by a metal spring (Figure 16). This will be useful, as it will show how the stress is diminished if the rubber deforms to any great extent.

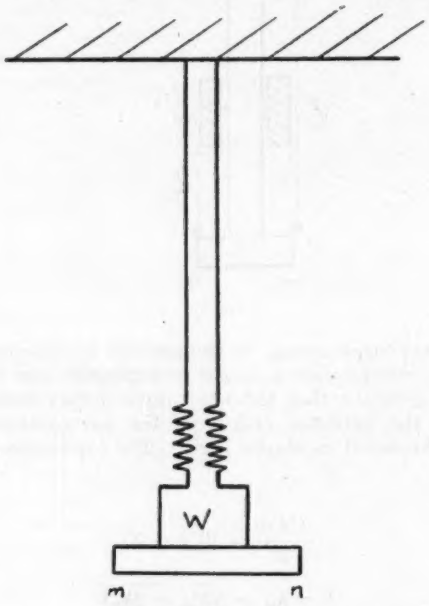


FIG. 16.

The weight W (30 lb.) has fallen through a height of 4 ft. The terminal velocity at mn is, therefore, 16 ft. per second.

l = free length of tube = 6 ft.
A = cross-sectional area of tube = 3 sq. in.
E = modulus of elasticity of tube = 10^7 lb per sq. in.
k = 2000 lb. = the force producing extension of the spring equal to 1 in.,

then:

$$\frac{\lambda^2 EA}{2l} - \frac{\lambda_{st}^2 EA}{2l} = \frac{W}{2g} V^2 + W(\lambda - \lambda_{st})$$

$$\frac{AE}{2l}(\lambda - \lambda_{st})^2 = \frac{WV^2}{2g}$$

The maximum extension becomes:

$$\lambda = \lambda_{st} + V\sqrt{\frac{Wl}{AEg}}$$

$$\lambda_{st} = \frac{Wl}{AE} = \frac{30 \times 6 \times 12}{3 \times 10^7} = 0.72 \times 10^{-4} \text{ in.}$$

Therefore, the stress during impact increases in the ratio:

$$\frac{\lambda}{\lambda_{st}} = 1 + \frac{V}{\sqrt{\lambda_{st} g}} = 1 + \frac{16 \times 12}{\sqrt{0.72 \times 10^{-4} \times 386}} = 1 + 1149 = 1150$$

Its magnitude is $\frac{30}{3} \times 1150 = 11{,}500$ lb. per sq. in. Note that with an increase of λ_{st} the effect of impact decreases. Now by putting the spring (or rubber) at the end of the tube, the static extension becomes:

$$\lambda_{st} = 0.72 \times 10^{-4} + \frac{30}{2000} = 150.72 \times 10^{-4}$$

In this case: $$\frac{\lambda}{\lambda_{st}} = 1 + \frac{16 \times 12}{\sqrt{150.72 \times 10^{-4} \times 386}} = 1 + 79.7 = 80.7$$

Its magnitude is $\frac{30}{3} \times 80.7 = 807$ lb. per sq. in. Admittedly the above mathematical treatment is not a rigorous one, but it is nevertheless useful. It shows how important it is to ensure that the speed of testing, *i.e.*, V the velocity of impact, be high enough to ensure that the rubber component is "frozen" and does not damp out the formation of the maximum stress. If this condition is not met, we see how in the hypothetical case described above, the stress at impact can be diminished by a factor of slightly more than 14.

APPENDIX II

In the construction of a falling-weight impact machine, one has to ensure that the supports are rigid and free from vibration. Let us now consider the extension of a system of two springs under impact load (Figure 17).

A system of two springs is suspended from a rigid support, and a mass m falling with velocity v causes extension of the system on impact. Ignoring the mass of the springs themselves, we can say that the static extension is zero.

Let the extension of spring 1 $= \lambda_1$

Let the extension of spring 2 $= \lambda - \lambda_1$

where λ = total extension.

Let the force required to extend spring 1 by 1 in. $= k_1$

Let the force required to extend spring 2 by 1 in. $= k_2$

Total elastic stored energy $= \frac{1}{2}k_1\lambda_1^2 + \frac{1}{2}k_2(\lambda - \lambda_1)^2$

Also $\frac{1}{2}k_1\lambda_1 = \frac{1}{2}k_2(\lambda - \lambda_1)$

$$k_2\lambda = (k_1 + k_2)\lambda_1$$

$$\lambda = \frac{k_1 + k_2}{k_2}\lambda_1$$

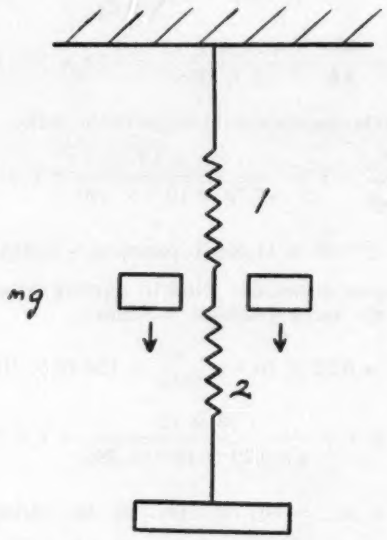


FIG. 17.

Energy absorbed in bringing the mass to rest is $\frac{1}{2}mv^2 + mg\lambda$. The term $mg\lambda$ corresponds to a further drop of λ after dropping several feet:

$$\therefore \frac{\frac{1}{2}mv^2}{mg\lambda} = \frac{\text{Height of fall}}{\text{extension}}$$

In general, therefore, we can ignore the second term:

$$\frac{1}{2}k_1\lambda_1^2 + \frac{1}{2}k_2\frac{k_1^2}{k_2^2}\lambda_1^2 = \frac{1}{2}\frac{\lambda_1^2(k_1k_2 + k_1^2)}{k_2}$$

$$= \frac{\lambda_{21}k_1(k_1 + k_2)}{2k^2} = \frac{1}{2}mv^2$$

$$\therefore \lambda^2_1 = \frac{mv^2k_2}{k_1(k_1 + k_2)}$$

$$\lambda_1 = v\sqrt{\frac{mk_2}{k_1(k_1 + k_2)}}$$

$$\lambda_2 = \lambda - \lambda_1 = \frac{k_1}{k_2}\lambda_1 = v\sqrt{\frac{mk_1}{k_2(k_1 + k_2)}}$$

The maximum load: $= k_1\lambda_1 = k_1 v \sqrt{\dfrac{mk_2}{k_1(k_1 + k_2)}}$

$$\therefore L = v\sqrt{\frac{mk_1k_2}{k_1 + k_2}}$$

If one spring, say spring 1, is rigid, then $k_1 = \infty$ and the maximum load $L\infty = v\sqrt{mk_2}$:

$$\frac{L}{L\infty} = \sqrt{\frac{k_1}{k_1 + k_2}}$$

If $\dfrac{L}{L\infty} = p$ and $\dfrac{k_1}{k_2} = \alpha$, it is possible to plot p against α, and this has been done in Figure 18. It will be seen that the stiffer the support in relation to the test-piece, the higher is the ultimate load.

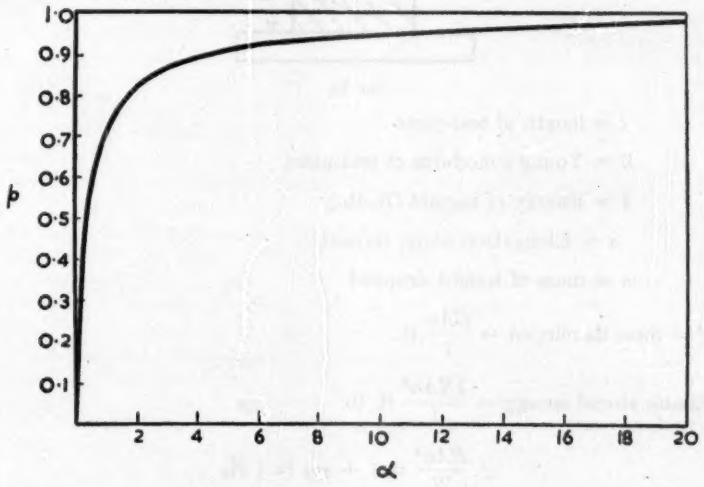


FIG. 18.

If k_2 = modulus (spring constant) of bonded test-piece:

$$\doteqdot 5 \times 10^3 \text{ lb. sq. in.}$$

k_1 = modulus (spring constant) of support $\doteqdot 10^6$ lb. sq. in.

$$\therefore \alpha \doteqdot 20$$

$$\text{and } p \doteqdot .98$$

which means that only 2 per cent of the maximum load is not developed.

APPENDIX III

EFFECT OF THE LENGTH OF THE TEST-PIECE ON THE BREAKING ENERGY

Making the following assumptions:

(1) The upper support is rigid, and

(2) The stress-strain properties of the test unit can be considered Hookean.

Let A = cross-sectional area (Figure 19).

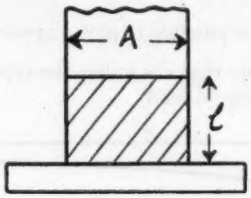


FIG. 19.

l = length of test-piece

E = Young's modulus of test-piece

I = Energy of impact (ft.-lb.)

α = Elongation under impact

m = mass of weight dropped

F = force developed $= \dfrac{EA\alpha}{l}$ lb.

Elastic stored energy $= \dfrac{\frac{1}{2}EA\alpha^2}{l}$ ft. lb.

$$\therefore \frac{EA\alpha^2}{2l} = 1 + m\alpha = \tfrac{1}{2}F\alpha$$

But $\alpha = Fl/EA$

$$\therefore I = \tfrac{1}{2}F \cdot \frac{Fl}{EA} - m\frac{Fl}{EA}$$

$$= \frac{Fl}{EA}\left(\frac{F}{2} - m\right)$$

Therefore if both the stress $S\left(=\dfrac{F}{A}\right)$ and Young's modulus E are independent of the length of the specimen, the energy of impact (I) which is just sufficient to break the specimen is proportional to the length of the test-piece.

For practical purposes m can be ignored in comparison with $F/2$, then:

$$I = \frac{F^2}{2EA} \cdot l = \frac{S^2A}{2E} \cdot l$$

This means that the energy of impact and the stress are governed by the volume of the unit and by the modulus of the unit.

REFERENCES

[1] Habgood, *Trans. Inst. Rubber Ind.* 13, 136 (1937).
[2] Charch and Maney, British patent 477,380 (1935).
[3] British patent 493,139.
[4] This cement was made in the laboratories at Blackley.
[5] Naunton, *Trans. Inst. Rubber Ind.* 24, 10 (1948).
[6] Murphy, Baker, and Reinhardt, *Ind. Eng. Chem.* 40, 2292 (1948).
[7] Roelig, Combined Intelligence Objectives Subcommittee Rept. XXXIII-9.
[8] Pittman and Thornley, *Trans. Inst. Rubber Ind.* 25, 116 (1949).
[9] American Society for Testing Materials. D429-47T.
[10] Rivlin, *Phil. Trans. Roy. Soc.* (London), Series A, 240, 459 (1948).
[11] Buist, *Trans. Inst. Rubber Ind.* 25, 262 (1949).
[12] Telfair and Nason, *Modern Plastics* 21, 85 (1943).
[13] Callendar, *British Plastics* 13, 445 (1942).
[14] Church and Daynes, *Trans. Inst. Rubber Ind.* 13, 96 (1937); British Electrical and Allied Industries Research Association, Technical Rept. B/S.4 (1945).
[15] Church and Daynes, *Trans. Inst. Rubber Ind.* 13, 96 (1937).
[16] Timoshenko and Lessells, "Applied Elasticity", Constable & Co., London, 1928.

DETERMINATION OF COPPER IN RAW MATERIALS USED IN THE RUBBER INDUSTRY *

J. GENOVA AND A. ADDOBBATI

RUBBER DIVISION OF THE DEPARTMENT OF CHEMISTRY, INSTITUTE OF TECHNOLOGICAL RESEARCH, SÃO PAULO, BRAZIL

Because of its catalytic action on the deterioration of rubber, the presence of copper in rubber products, even in very small quantities (0.001 per cent), may lead to serious difficulties which shorten the useful life of the products.

Most of the raw materials used in the manufacture of these products contain small percentages of copper, and its determination is best made by the colorimetric method.

Various reagents can be used for this purpose, among them dithizone (phenylazothionoformic acid phenylhydrazide) and sodium diethyldithiocarbamate. The use of the latter was proposed by Callan and Henderson[1]. The method specified by the A.S.T.M.[2] for the determination of copper in rubber products is based on their work. This method may be briefly described as follows.

The destruction of the organic matter and dissolution of the sample is effected by digestion with sulfuric acid in a Kjeldahl flask, followed by treatment with fuming nitric acid and hydrogen peroxide. Repeated treatment and final evaporation to the point where white fumes are evolved eliminates any colored substances and any excess of oxidizing agents. The sesquioxides are precipitated by ammonium hydroxide, and an aliquot part of the filtrate obtained is transferred to a Nessler tube. One cc. of 5 per cent solution of gum arabic, 10 cc. of ammonium hydroxide (d. 0.90), and 10 cc. of 0.1 per cent solution of sodium diethyldithiocarbamate are added. The presence of copper is indicated by the formation of its gray colored carbamate, which, because of its colloidal nature, remains in suspension.

A blank sample containing all the reagents used is placed in another Nessler tube, and the same analytical procedure is followed. Small quantities of a test solution of copper (0.00001 g. per cc.) are added by means of a burette until the intensity of the color of the blank becomes the same as that of the sample being analyzed. The amount of standard copper solution added is proportional to the quantity of copper in the sample.

The same method may be employed for the determniation of copper in crude rubber and in organic compounding ingredients and, with slight modifications in that part of the procedure concerned with the solution of the sample, for its determination in inorganic compounds[3].

In a series of analyses of such new materials by the method described above, various difficulties were encountered. In some cases, after the addition of the carbamate, a complication was observed which interfered with the determination. This difficulty is due to the presence of salts of zinc, lead, and other metals, which precipitate during the reaction.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Anais da Associação Química do Brasil*, Vol. 7, No. 4, pages 204–207, December 1948, by Alan Davis.

Palfrey, Hobert, Benning, and Dobratz[4] have suggested various methods of eliminating these interefering cations. In the analyses carried out in this laboratory, the trouble was overcome by the simple addition of a greater excess of ammonium hydroxide.

In the analysis of certain fillers (clay, calcium carbonate, etc.) with relatively high percentages of manganese, the solution on treatment with the carbamate became violet color, and this made it impossible to determine the copper colorimetrically.

The interference of manganese has already been observed by various authors[5]. Cassagne[6] proposed the separation of manganese, iron, zinc, and heavy metals by hot precipitation with disodium phosphate in ammoniacal medium. Experiments carried out in this laboratory, however, demonstrated that, according to the method described by Cassagne, the elimination of manganese is not complete, and the resulting solution still shows a violet color.

Hillebrand and Lundell[7] observed that, even when the precipitate is allowed to stand for a relatively long time, the filtrate still may contain up to 0.3 mg. of manganese. Because of the intense color produced with the carbamate, even this small quantity interferes with the determination of copper.

Another means of avoiding interference by manganese would be to separate copper by precipitation with hydrogen sulfide, according to the method described by Ansbacher, Remington, and Culp[8]. However, in addition to being unreliable[9], this method is very slow.

Still another way of avoiding interference by manganese is to precipitate it in ammoniacal medium by the addition of strong oxidizing agents (bromine water, etc.). This treatment, however, must be carried out with certain precautions in order to obtain complete precipitation[10]. In experiments carried out in this laboratory, we succeeded in eliminating any interference by manganese by heat treatment of the slightly ammoniacal solution with bromine water, and then making it alkaline with ammonium hydroxide. This treatment is repeated until all the manganese is precipitated.

The data in Table I show the results obtained in the determination of copper by the diethyldithiocarbamate method in solutions containing manganese and other cations, previously treated with bromine in ammoniacal solution.

TABLE I

Cations in solution (mg.)					Copper (mg.)
Pb	Mn	Fe	Zn	Cu	Values determined
8	3	—	–	18	17
8	3	—	–	17	18
8	3	—	–	12	12
8	3	—	–	5	7
8	3	1.6	4	10	9.5

Table II records the percentages of copper found by this method in various raw materials before and after the addition of known quantities of copper.

TABLE II

Material	% Cu determined originally	% Cu added	Total % Cu	% Total Cu determined
Kaolin	0.0015	0.005	0.002	0.002
Virgin Seramby rubber	0.0028	0.0010	0.00038	0.004
Fine Accra rubber	0.0030	0.0010	0.004	0.004

In conclusion, the data given seem to indicate that the proposed modification makes it possible to determine copper in the presence of manganese by the A.S.T.M. method with a precision which is within the limits of error of colorimetric methods. Interference by manganese is eliminated by a simple and rapid method.

REFERENCES

[1] Callan and Henderson, *Analyst* **54**, 650 (1929).
[2] American Society for Testing Materials, Standards on Rubber Products, 29 (1944), D297-43T.
[3] Dekker, RUBBER CHEM. & TECHNOL. 11, 706 (1938).
[4] Palfrey, Hobert, Benning, and Dobratz, *Ind. Eng. Chem. Anal. Ed.* 12, 94 (1940).
[5] Sandell, "Colorimetric Determination of Traces of Metals," New York, 1944, p. 222.
[6] Cassagne, RUBBER CHEM. & TECHNOL. 20, 308 (1947).
[7] Hillebrand and Lundell, "Applied Inorganic Analysis", New York, p. 349.
[8] Ansbacher, Remington, and Culp, *Ind. Eng. Chem. Anal. Ed.* 3, 314 (1931).
[9] Sandell, "Colorimetric Determination of Traces of Metals", New York, 1944, p. 214.
[10] Treadwell and Hall, "Analytical Chemistry", New York, 1937, Vol. 2, p. 222.

POLAROGRAPHIC DETERMINATION OF ZINC IN COMPOUNDED RUBBER *

F. C. J. POULTON AND L. TARRANT

DUNLOP RUBBER CO., LTD., ERDINGTON, BIRMINGHAM, ENGLAND

INTRODUCTION

The present investigation was undertaken primarily in connection with a factory problem in which the rapid determination of small amounts of zinc in vulcanized rubber was of paramount importance. The amount of sample available was sometimes as much as 0.5 gram, but usually less than this, and the proportion of zinc anticipated (as oxide) was of the order of 0.1 per cent.

Experience with the gravimetric process in which the zinc is weighed as pyrophosphate, and with the usual volumetric method of titrating the zinc solution with potassium ferrocyanide, clearly demonstrated the deficiencies of these methods both in respect of time and accuracy. These shortcomings arise mainly from the necessity of removing interfering substances from the ash of the rubber before precipitating the zinc as sulfide, and also, in the case of the volumetric method, from the fact that the titration with potassium ferrocyanide of reasonable concentration may lead to considerable error when the amounts of zinc are so small. Dilution of the titrant results in making the end-point less definite.

8-Hydroxyquinoline (oxine) is a more satisfactory reagent for zinc at fairly low concentrations, and is capable of precipitating a few milligrams of zinc when the operations are reduced to the microscale. It still remains necessary in many cases, however, to isolate the zinc from interfering metals by, for example, a preliminary sulfide separation, and the saving of time over the whole process, therefore, is not great[1].

It was apparent in view of the foregoing considerations that the polarographic technique offered the greatest promise, and the method finally adopted, besides estimating small quantities, was found to deal adequately with much larger proportions. The method now recommended is applicable to the determination of zinc over the whole range in which it is likely to be encountered in normal rubber analysis.

EXPERIMENTAL WORK

A study of the literature shows that there are numbers of alkaline and acid base solutions which in appropriate circumstances are suitable for the polarographic estimation of zinc[2]. Unless metals of the analytical Groups II and III are absent, however, alkaline solutions may give rise to precipitates which influence the magnitude of the diffusion current. Furthermore, in cases where the zinc content is low, serious error is introduced by the precipitation of zinc by phosphates arising originally from the rubber. It is an unfortunate circumstance that in latex mixings when an accurate knowledge of the zinc content is of importance, errors from this source can reach relatively large proportions.

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 25, No. 5, pages 328–333, February 1950.

From a consideration of a representative selection of compounded rubber stocks it became evident that the influence of the following metals (apart from others less commonly occurring) would need to be investigated in relation to the polarographic behavior of zinc: calcium, barium, magnesium, aluminum; antimony, titanium; lead, cadmium; iron.

Calcium, barium, magnesium, aluminum.—Electroreduction of these metals is effected at a negative potential well above that of zinc, and they need be considered only from the standpoint of their chemical reactivity with the base solution.

Antimony, titanium.—Titanium oxide is not soluble in hydrochloric acid or acetic acid, and antimony oxide, initially dissolved, is reprecipitated as the oxychloride on dilution with the base solution. Use of these acids for extraction of zinc from the ash of a compounded rubber will, therefore, eliminate these metals as sources of major interference. By tracing polarograms of a standard solution before and after the addition of a hydrochloric acid extract of antimony and titanium oxides, it was shown that the zinc wave remained substantially unchanged in height and form.

Lead, cadmium.—Both these metals often occur in small proportions as impurities in "rubber grade" zinc oxide, and also find some use as compounding ingredients, the former as oxide and the latter as sulfide or selenide. Supporting electrolytes can be chosen in which the three waves can be sufficiently well separated to allow for the simultaneous estimation of these metals.

Thus in an ammonia-ammonium chloride electrolyte, the half-wave potentials against the mercury anode are:

Zinc	−1.0 volt
Lead	−0.4 volt
Cadmium	−0.57 volt

Iron.—Iron in the form of oxide is frequently added to compounded rubber as a pigment, but also forms an impurity in many components of the mixing. Ferric iron gives an ill-defined wave in many electrolytes, and it becomes necessary to remove it when the zinc content is small. Unfortunately, when iron is precipitated as ferric hydroxide the error arising from the coprecipitation of zinc can be serious and it has not been possible to substantiate the views of some workers that the presence of ferric and aluminum hydroxides does not interfere with the normal polarogram. Thus the wave height of a solution of 10 mg. of zinc in an ammonium chloride-ammonium hydroxide base solution was reduced in the presence of 10 mg. of ferric iron by about 4 per cent.

Inhibition of the precipitation of ferric hydroxide by the addition of citric acid was also considered as a means of overcoming these difficulties, but in this medium a triple wave was produced. Although the middle portion of this curve corresponded reasonably closely to the known zinc concentration, the third wave, presumably due to the reduction of an iron complex, so closely approached the zinc wave that accurate measurement became uncertain.

Table 1 represents the results obtained on a series of laboratory mixed samples of compounded rubber, and demonstrates the discrepancy between the oxine gravimetric method and the polarographic method using an ammonium chloride-ammonium hydroxide electrolyte with gelatin as maximum suppressor. The amounts of added zinc oxide are nominal only, owing to the difficulty of making accurate small-scale rubber mixings.

The samples of compounded rubber referred to in Table 1 were purposely kept simple in character, and the ferric hydroxide present, if any, arose only from extraneous iron and consequently was extremely small in amount.

Samples of rubber containing less than 1 per cent of zinc oxide were not examined systematically in this electrolyte because of the possibility of precipitating zinc as phosphate, as has already been explained. It is of interest perhaps to mention in this connection that a sample of latex, to which 0.01 per cent of zinc oxide had been added, failed completely to give an indication of zinc when examined polarographically in an alkaline electrolyte.

TABLE 1

Sample no.	ZnO added (nominal) (per cent)	ZnO by estimation	
		Oxine method (per cent)	Polarographic method (per cent)
1	1	1.12	1.04
2	1	1.13	1.06
3	8.25	8.18	7.93
4	8.25	8.13	8.04
5	15.5	15.21	15.01
6	15.5	15.21	15.21
7	30	30.07	29.87
8	30	30.39	30.37

Attention was then turned to the use of acid or neutral base solutions to avoid the difficulties already outlined.

The most common feature of the polarogram from the use of acid electrolytes is the considerable positive shift that the hydrogen wave undergoes, often making accurate measurement of the wave height of zinc a matter of some difficulty. Thus 0.1 *N* hydrochloric acid gives a hydrogen wave which merges completely with the zinc wave. Using potassium chloride as the supporting electrolyte and depressing the pH value with either hydrochloric or acetic acid, provides some improvement, but the separation still remains insufficient for accurate measurement. Interference from iron was suppressed in these cases by adding sodium fluoride to the solution. The relatively stable ferri-fluoride complex thus formed is only reduced at a potential of −1.36 volt.

Experiments were then carried out with a base solution containing ammonium acetate, ammonium phosphate, and acetic acid. In such a solution iron and aluminum are precipitated but zinc remains in solution. An excellent wave was obtained with zinc alone in this solution, but when iron and aluminum were also present, there was a marked reduction in the wave height, presumably due to coprecipitation of the zinc. Also, when the solution was made too acid, separation between the zinc and hydrogen waves was poor. This effect was again experienced when hydroxylamine hydrochloride was used to eliminate the interference of iron by reducing it to the ferrous condition, but by the use of potassium iodide it was possible to reduce the iron without influencing the position of the hydrogen wave. Use was made of this feature in the method finally adopted, which also has the advantage that, in the electrolyte used, lead and cadmium can be determined concurrently with the zinc.

A point to note is that addition of potassium iodide caused the half-wave potentials of lead, cadmium and zinc to shift positively by about 0.2 volt.

The method has been in use for several months and so far no difficulties have been encountered.

Experimental details.—Weigh a sample of the compounded rubber into a porcelain crucible and heat carefully to remove all organic matter. Add 0.5 cc. concentrated hydrocholoric acid to the ash, heat just to dryness, moisten with dilute acetic acid (equal volumes glacial acid and water) and dilute with a

few cc. of warm water. Boil the solution with 2 cc. of 5 per cent aqueous potassium iodide solution until the brown color of any liberated iodine is discharged, cool and transfer to a 50-cc. standard volumetric flask containing 10 cc. of the following base solution:

Potassium thiocyanate	24 grams	made up to 1 liter with water
Ammonium acetate	76 grams	
Methyl red sodium salt (0.02 per cent soln.)	25 cc.	
Gelatin (1 per cent aqueous solution)	20 cc.	

If necessary, adjust the pH of the solution to a value of 4–5 by adding acetic acid until the methyl red is just red, then dilute with water to standard volume. The solution is then ready for polarographing. After the removal of dissolved oxygen by bubbling pure nitrogen through the cell for 5 minutes, polarograph the solution over the voltage range −0.5 to −1.2 volt.

Standard calibration curves are prepared by treating similarly zinc oxide of analytical quality.

To test the validity of the proposed method, three series of test compounds were prepared, representing in zinc oxide content three typical classes of commercial rubber products, *viz.*:

(1) 15–40 per cent zinc oxide where high resilience stocks are required (*e.g.*, some mechanicals and tire-casing compounds).
(2) 2–5 per cent zinc oxide compounds, representing stocks in which the main function of the zinc oxide is to activate the accelerator of vulcanization.
(3) Less than 1 per cent zinc oxide in latex mixings, in which the zinc is introduced often as zinc-containing accelerator of the zinc diethyldithiocarbamate type.

In the cases of series A and series B, the samples were prepared by mixing on a laboratory mill weighed quantities of zinc oxide of known purity into the following stocks:

	Stock A	Stock B
Smoked sheet rubber	100	100
Sulfur	3	3
Stearic acid	2	2
Mercaptobenzothiazole	1	1
China clay	15	—
Calcium carbonate	—	15
Iron oxide	—	8
Lamp black	15	—

Where low concentrations of zinc oxide are required, however, the dry mixing technique tends to give uneven dispersion, and in series C, therefore, the samples were prepared by introducing known quantities of zinc diethyldithiocarbamate dispersion, whose composition with respect to zinc content was known, into stabilized natural-rubber latex concentrate. After some minutes' stirring, the mixture was run onto a horizontal glass plate, and allowed to dry at about 30° C, stripping and reversing the film after about 12 hours' drying. To effect final drying and to ensure uniformity, the sample film was sheeted thinly on a laboratory mill.

Results obtained on these samples are shown in Table 2.

As would be anticipated, the precision of the method applied to the higher ranges is not so high as would be obtained by the normal gravimetric procedure (*e.g.*, by precipitation with 8-hydroxyquinoline). This is due to the inherent

TABLE 2

	Zinc oxide added Per cent	Zinc oxide found: Stock A (Per cent)	Zinc oxide found: Stock B (Per cent)
Series A	40	39.7	38.9
	30	30.2	30.2
	20	20.1	19.9
	15	14.8	14.6
Series B	5	4.93	5.03
	4	3.91	3.95
	3	2.98	3.10
	2	1.96	2.06
	Zinc diethyldithiocarbamate added	Zinc diethyldithiocarbamate found (duplicate determinations)	
Series C	1.41	1.38	1.40
	1.02	1.02	1.01
	0.85	0.83	0.83

error in polarographic measurements, and is manifested particularly in the determination of major components.

In series B the precision of the results is of the same order as that obtained by gravimetric methods, and for routine testing purposes this is usually adequate. The time occupied in the polarographic method is much less than in the former methods when applied to compounds whose mineral content is of such a nature that some degree of analytical separation is normally necessary. After completion of the ashing stage, the proposed method takes approximately one hour for estimation of zinc content.

CONCLUSION

The inaccuracies associated with the phosphate precipitation method and the potassium ferrocyanide titration method for the determination of small quantities of zinc in compounded natural rubber arise from two main sources: (1) coprecipitation of zinc with ferric and aluminum hydroxides during the removal of these substances in the course of the normal analytical group separation; and (2) precipitation of the zinc by phosphate arising originally from the rubber.

A polarographic method has been developed in which both interfering factors are obviated by carrying out the electrolysis in an acid medium. It is applicable to the complete range in which zinc is likely to be encountered in rubber analysis (0.05–40 per cent). The degree of accuracy attainable is about ±2 per cent of the figure reported; consequently the method finds its greatest usefulness at lower zinc oxide contents, *i.e.*, in the region where the older analytical methods begin to fail.

The prior removal of other metallic constituents of the ash is unnecessary, and a preliminary separation of the zinc as sulfide is avoided. This feature permits a considerable saving of time: commencing with the ash from a rubber compound, the determination by the polarographic method may be completed within an hour, and a reasonable number (say up to six) determinations can be carried through concurrently.

SUMMARY

Reasons are advanced for the unsatisfactory nature of some of the older methods for the determination of very small amounts of zinc in compounded rubber, particularly in latex mixings.

The polarographic technique offers a possible solution, but most of the commoner electrolytes for the electroreduction of this metal are alkaline, and give rise to similar errors as are met in the gravimetric procedure. The development of a suitable acid electrolyte was therefore undertaken, and ways of dealing with likely interferences were examined. The electroltye finally recommended is a potassium thiocyanate-ammonium acetate buffer solution; iron, when present, is reduced to the ferrous condition by potassium iodide.

The method was used to determine zinc oxide in a series of mixings of known composition ranging from 0.8 to 40 per cent. In all except the highest proportions of zinc oxide, the figures obtained agree well with the theoretical.

REFERENCES

[1] Fleck and Ward, *Analyst* **58**, 388 (1933); Loyer and Remington, *Ind. Eng. Chem. Anal. Ed.* **10**, 212 (1938).
[2] Kolthoff and Lingane, "Polarography", Interscience Publishers, Inc., New York, 1941, p. 271.

MECHANICAL STABILITY TEST FOR HEVEA LATEX *

H. G. DAWSON

THE FIRESTONE TIRE & RUBBER COMPANY, AKRON, OHIO

Hevea latex is a complex, collidal suspension that is continually changing with age, temperature, agitation due to centrifuging or transportation, preservatives, and addition of compounding ingredients. Ever since latex became an article of commerce, the need has been recognized for a quick reliable test of the colloidal stability of a given sample.

Three general approaches have been made to this problem of measuring the stability of latex: mechanical, chemical, and heat. The first method is based on the application to the latex particles of a mechanical shear by rapid stirring, slow stirring, shaking, or rubbing. Chemical stability involves the addition of a "sensitizing" agent such as zinc oxide, ammonium sulfate, calcium sulfate, or sodium silicofluoride to the latex, and measurement of its effect by the resultant increase in viscosity or decrease in mechanical stability; while heat involves thermal agitation of the latex particles as well as possible changes in the coating on the particles.

Although many tests have been devised which are based on one or more of these approaches, the simplest and most efficient in time and sensitivity is the mechanical stability test. This test, as generally run with a high-speed stirrer, has been more or less generally accepted as a standard test, but there is some question as to whether it gives a completely accurate index of the stability under conditions that prevail in ordinary handling operations. It has been widely used in various forms for a number of years, and no doubt a number of studies have been made on the effect of different variables, but no publication attempting to summarize such studies has appeared in the literature.

In 1930, Morris[1] used a Hamilton Beach drink mixer "to compare the stabilities of the various latices when subjected to vigorous agitation". Several investigators had made exploratory experiments with the method before 1930, but the first published account of a high-speed stirring test for the estimation of latex stability was given by Noble[2] in 1936. He specified a Hamilton Beach mixer, a 118-cc. (4-ounce) square bottle, and a 50-gram sample at 30 per cent total solids. Noble also stated that the addition of 7 per cent zinc oxide decreases the (mechanical stability) time by one-half. This is the first mention of a combined mechanical and chemical stability test where some chemical such as zinc oxide is added to sensitize the latex. In 1937, Jordan[3] included a mechanical stability test, using a Hamilton Beach drink mixer, in a list of proposed physical testing methods for the examination of rubber latex and rubber latex compounds. Murphy[4] devised a test apparatus which was designed to reproduce under controlled conditions the hand rubbing test in which coagulation is brought about mainly by the combined influence of friction and evaporation. It consisted of a molded rubber nose as a rubbing element, which rotated with a sun and planet motion over a glass plate on which the latex sample was spread.

* Reprinted from *Analytical Chemistry*, Vol. 21, No. 9, pages 1066–1071, September 1949. This paper was presented at the 53rd meeting of the Division of Rubber Chemistry at Detroit, Michigan, November 8–10, 1948.

The end point was defined as the number of seconds for the film to commence to break up into small particles of coagulum.

Davey and Coker[5] objected to the high-speed stirring test on the basis that it tends to break up the coagulum as it is formed; hence, they proposed a tester having a cylindrical (5×2 cm., $2 \times \frac{13}{16}$ inch diameter) impeller, with three vertical fins, rotating at 2000 r.p.m. As the total solids were reduced to 30 per cent, which increases the mechanical stability greatly, it was necessary to

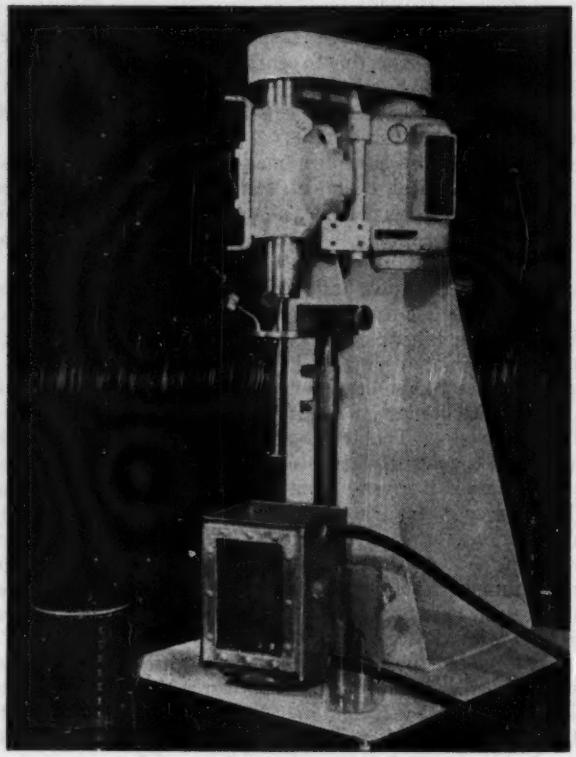


FIG. 1.—Mechanical stability tester.

sensitize the latex by the addition of 50 per cent dry zinc oxide based on the dry rubber content. Martin[6] substituted sodium fluosilicate for zinc oxide in the test.

Novotny and Jordan[7] further improved the mechanical stability test by employing a constant speed motor and controlling the solids very carefully. In 1940, the Crude Rubber Committee[8] of the Division of Rubber Chemistry, AMERICAN CHEMICAL SOCIETY, proposed a standard procedure for determining the mechanical stability of latex L-13. No further improvements have been made since that time, and each user has made his own adaptation of the procedure. All this emphasizes the need for further study of the many variables and rigid standardization of the test.

APPARATUS

The test apparatus (Figure 1) is essentially a vertical shaft, high speed stirrer capable of maintaining a constant speed of 14,000 r.p.m. for the duration of the test.

The mechanical components consist of a Dumore grinder No. 5 (The Dumore Co., Racine, Wis.) equipped with a special quill designed for vertical rather than horizontal operation. Different speeds were obtained by using a Variac in the universal motor circuit, and the speed of the spindle was accurately measured with a Strobotac or a Jaeger portable tachometer. This arrangement was necessary for the study of the test at various speeds, but it is not recommended as standard equipment. For routine testing, the equipment should have only one speed. Induction motor drive will deliver constant shaft speed at low load despite minor variations in line voltage.

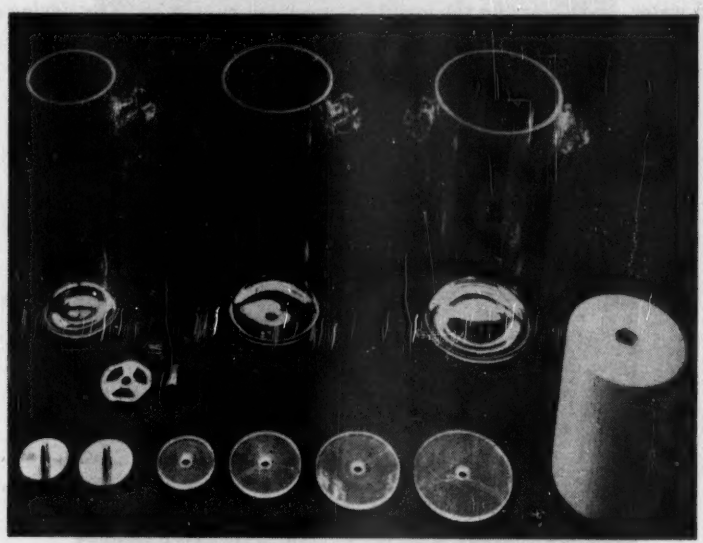


FIG. 2.—Propellers and bottles used in mechanical stability determinations.

The stirrer shaft or spindle is 0.6 cm. in diameter, although this is apparently not significant, as it rotates in a vortex of air. A Benedict drink mixer ring-type agitator (Figure 2) has been widely used for some ten years, but its irregular shape makes it difficult to reproduce; hence, a plain polished stainless steel disk 0.844 inch in diameter and 0.0625 inch thick is now proposed as a standard agitator. Extensive tests indicate that this simple disk yields results comparable numerically with those obtained with the old standard.

The bottle employed in these tests is a flat-bottomed cylindrical glass container $2\frac{5}{32}$ inches in inside diameter by approximately 5 inches high (Figure 2). These were made directly from Pyrex tubing having an inside diameter of $2\frac{5}{32}$ inches (55 mm.).

The bottle holder is so constructed that the bottle may be conveniently lowered or raised until the agitator is any desired distance from the bottom of the bottle and exactly in the center.

Constant temperature of the sample is maintained by a water tank with a window as shown in Figure 1.

PROCEDURE

Dilute the latex to exactly 51.5 per cent total solids (50 per cent dry rubber content) with distilled water. Place 80 cc. of the diluted latex in the test bottle, adjust the temperature of the latex to 35° C, and place in position for stirring at 14,000 r.p.m. The mechanical stability is arbitrarily defined as the time in seconds required to coagulate or agglomerate 0.5 to 1 per cent of the total solids as measured by filtering the latex through fine cheesecloth, washing with distilled water, and observing the quantity of coagulum (Figure 3) by drying and

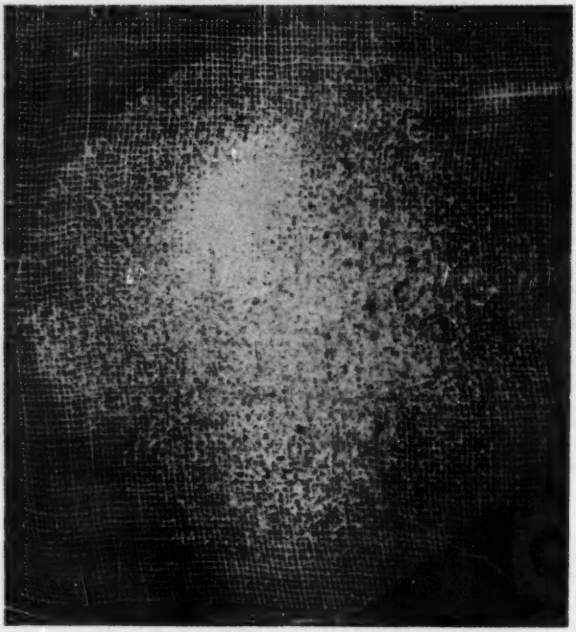


FIG. 3.—Appearance of latex coagulum on cheesecloth at end point.

weighing. This determination of the end point is accurate and is an essential part of the procedure, at least until the operator becomes skilled at estimating the end point by the visual method described below.

The approach to the end point can usually be noted visually by a drop of the meniscus of the latex due to foam collapse (Figure 4) and loss of turbulence. Dip a glass rod into the latex and draw it across the palm of the hand (clean and moist); the presence of small flocs of coagulum is evident at the end point, as can be further shown by filtering the latex through cheesecloth. One can also introduce a drop of latex onto a large surface of distilled water in a Petri dish or watch glass. The latex immediately spreads out into a large film which permits easy inspection for minute flocks present at the end point.

FACTORS AFFECTING THE TEST

Speed of stirring.—The greater the speed of stirring, the less the time required to reach a given degree of coagulation of the end point (Figure 5). A Benedict ring-type propeller ($\frac{15}{16}$-inch diameter) was used in all these determinations. All latices used were commercial ammoniated concentrates (61 to 62 per cent total solids) designated by letters *A* to *T* in Figures 5 to 13. Ab-

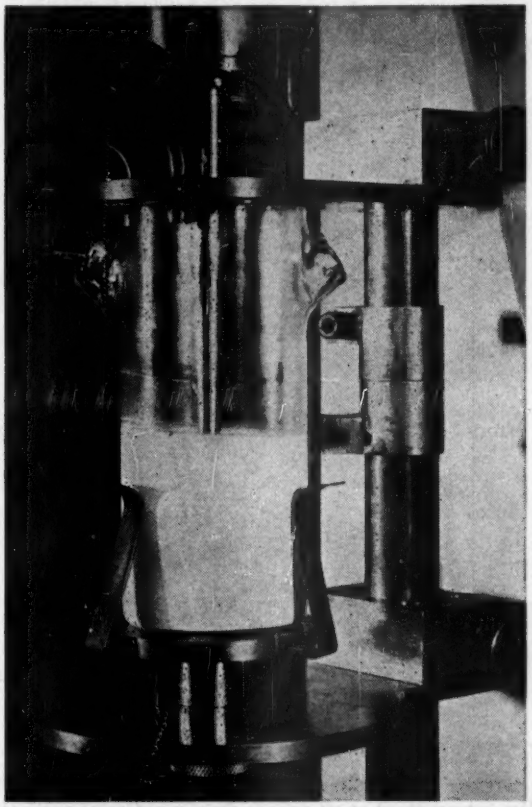


FIG. 4.—Meniscus fall due to foam collapse as test approaches end point.

normally high mechanical stability time values obtained at speeds below 8000 r.p.m. can be explained by assuming that at low speeds the shear has been reduced below the minimum required to overcome the repulsive forces between the latex particles.

Diameter and thickness of propeller.—A series of stainless steel and plastic disks varying in diameter from 0.75 to 1.47 inches (Figure 2) was used at 14,000 r.p.m. in testing several latices. Mechanical stability time is inversely proportional to the diameter of the agitator at a given shaft speed (Figure 6). However, as the diameter is decreased below 1 inch the mechanical stability

time increases at a far greater rate, giving a region of maximum sensititivy but less reproducibility.

When the thickness of a given agitator was increased 500 per cent, the mechanical stability time of latex B decreased only 16.3 per cent; hence, the thickness of the propeller appears to be far less significant than the diameter under these conditions.

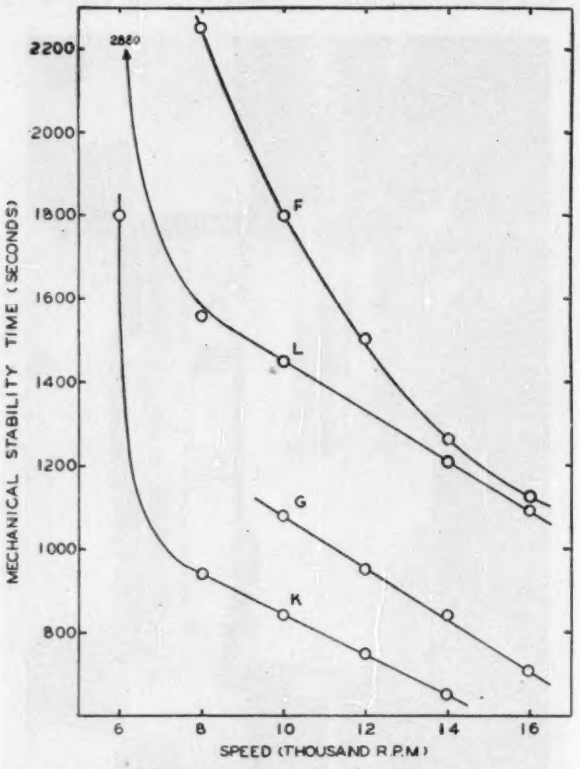


FIG. 5.—Effect of speed of stirring on mechanical stability time.

Speed vs. diameter of propeller.—Decreasing the shaft speed or the diameter of the propeller (at constant shaft speed) decreases the peripheral speed of the propeller. Decreasing the peripheral speed causes a proportional increase in the mechanical stability time value until a minimum peripheral speed of approximately 50 feet per second is reached. Below this peripheral speed mechanical stability time values become abnormally high. When a 1-inch propeller was run at 10,000 r.p.m., the peripheral speed was 43.6 feet per second and the mechanical stability time for latex B was 2040 seconds; when the shaft speed was increased to 12,000 r.p.m., the peripheral speed became 52.4 feet per second and the mechanical stability time decreased from 2040 to 825 seconds. When the shaft speed was kept constant at 10,000 r.p.m. but a larger propeller of 1.25-inch diameter was used, the peripheral speed was 54.5 feet per second and the mechanical stability time decreased from 2040 to 720 seconds. Further

increases in shaft speed or diameter of propeller caused regular and small decreases in mechanical stability time for this latex. It is probable that this minimum peripheral speed represents the shear required to overcome the electrostatic repulsive forces between the latex particles.

Low speed-high shear stability test.—A wood cylinder 2 inches in diameter by 3 inches high (Figure 2) was mounted on the test shaft in place of the regular propeller. Speeds of 3000 to 4000 r.p.m. gave very high mechanical stability time values, although the shear was sufficient to raise the temperature of the

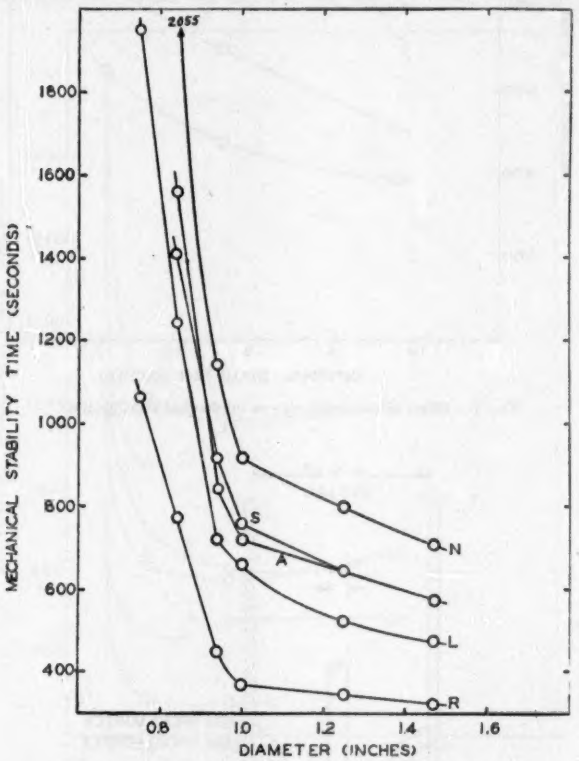


FIG. 6.—Relation of propeller size to mechanical stability time.

sample from 25° to 50° C. This can be explained by assuming that a minimum peripheral speed of approximately 50 feet per second must be attained. A cylinder 2 inches in diameter would have to rotate at a speed of 6000 r.p.m. to reach this peripheral speed. When the shaft speed was increased to 5000 r.p.m. a normal sequence of meniscus fall followed by a definite end point was obtained in 300 seconds, compared to 1285 seconds for the same latex when run under standard conditions. High shear decreases the mechanical stability time markedly if the peripheral speed reaches a minimum of 50 feet per second.

Diameter of test bottle.—Decreasing the diameter of the test bottle (perfectly round and smooth internally) decreases the mechanical stability time to a small

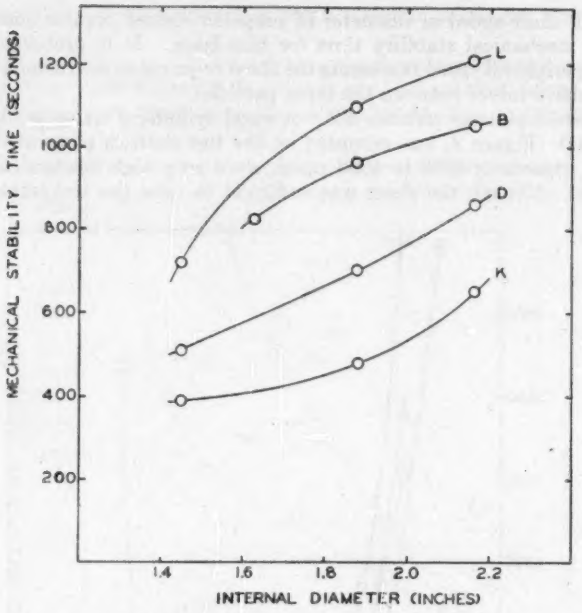


FIG. 7.—Effect of test bottle size on mechanical stability time.

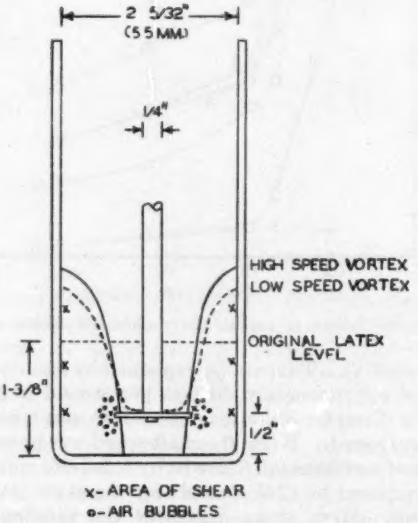


FIG. 8.—Cross-section diagram of mechanical stability test.

extent (Figure 7), but the rate of decrease becomes greater as the inside diameter of the test bottle approaches the diameter of the propeller. Because these changes are still small compared to the change in mechanical stability time obtained by changing the diameter of the propeller (Figure 6), it is concluded that most of the shear or rub takes place at the edge of the propeller rather than at the bottle wall (Figure 8).

Shape and inside surface of test bottle.—The rub or shear between the latex and the bottle is at a minimum when the bottle is perfectly round and smooth. When the standard test bottle was lined with 0.25-inch mesh hardware cloth the

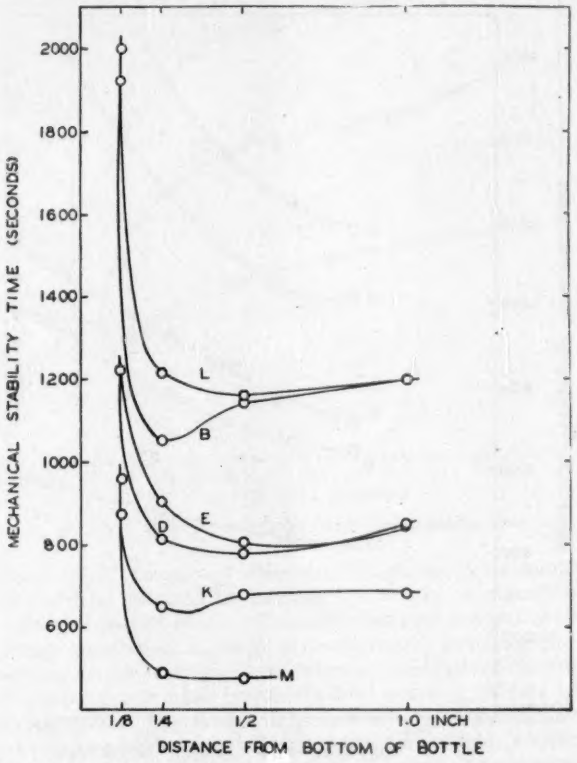


FIG. 9.—Relation of mechanical stability time to distance of propeller from bottom of test bottle.

mechanical stability time for a given latex decreased from 1050 to 600 seconds, indicating that the total shear had increased almost 50 per cent. Roughening the inside surface or changing the shape of the bottle increases the shear at the wall and decreases the mechanical stability time for the latex.

Distance of propeller from bottom of test bottle.—The mechanical stability time should decrease as the distance between the propeller and the bottom of the test bottle is decreased if the shear or rub takes place between the bottom of the propeller and the bottom of the test bottle. However, Figure 9 shows that there was little change in mechanical stability time when the propeller was

lowered progressively from 1 inch to 0.5 inch, to 0.25 inch from the bottom. Decreasing the distance to 0.125 inch from the bottom of the test bottle gave marked increases in mechanical stability time values; this indicates that the shear had been decreased rather than increased. Consequently, the test should not be run with the propeller less than 0.25 inch from the bottom of the test bottle, and the magnitude of any possible errors would be decreased if the distance was increased to 0.5 inch.

Size of sample.—With all other conditions constant, the larger the sample of a given latex the greater the mechanical stability time value (Figure 10).

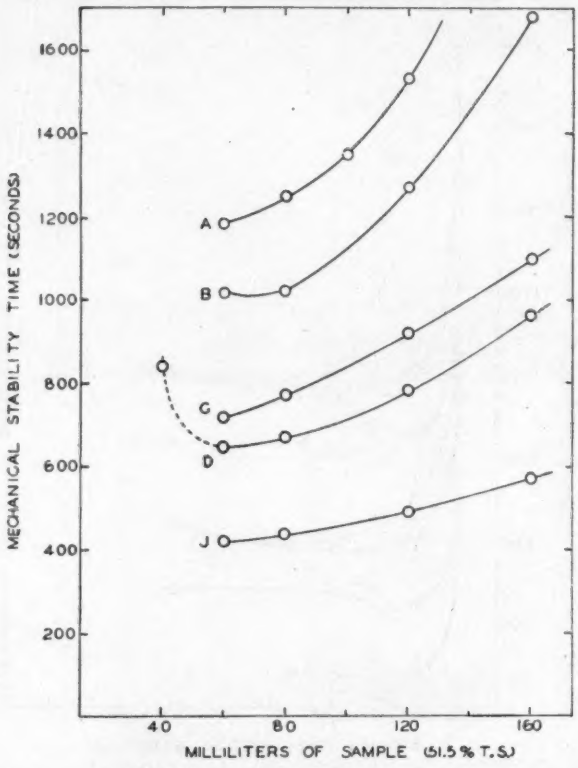


FIG. 10.—Effect of latex sample size on mechanical stability time.

When the sample size was reduced to 40 cc., abnormal results were obtained, indicating that the rate of shear as well as the sample size had been decreased.

The rate of change of mechanical stability time with an increase in sample size is greater for a high stability latex than one of low stability. This phenomenon has been noted for several of the other factors studied, and indicates a measure of the probability that two particles will stick together upon collision. Assuming constant shear, the probability depends upon the nature, extent, and degree of hydration of the coating or interfacial film on the individual latex particles.

Ammonia concentration.—Ammonia concentrations greater than 0.4 per cent have little effect on the mechanical stability of latex (Figure 11), but concentrations below this figure represent a greater drop in pH and a corresponding more rapid drop in mechanical stability time is observed. Here again, the rate of change of stability time for a high stability latex is much greater than the rate for a low stability latex.

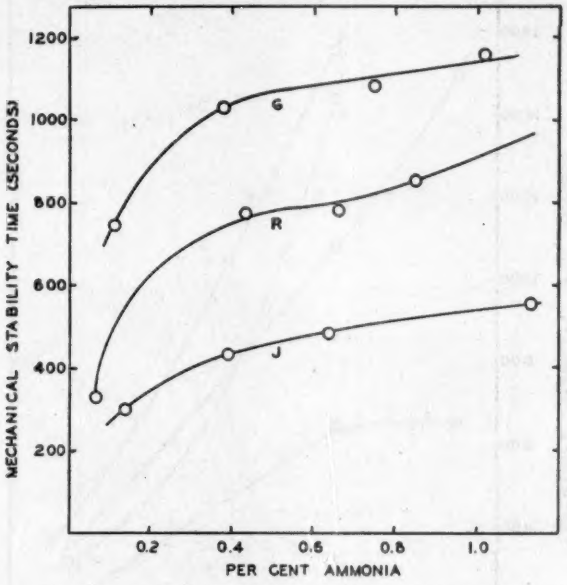


FIG. 11.—Ammonia concentration *vs.* mechanical stability time.

Replacement of air by oxygen or nitrogen.—No change in mechanical stability time values could be obtained by running the test in an atmosphere of pure oxygen or nitrogen instead of air. This indicates that the test involves only a physical change rather than a chemical reaction such as oxidation.

Total solids of sample.—At high total solids concentrations (61 to 62 per cent) all natural latices tend to have low mechanical stability (Figure 12). As the total solids is decreased, the stability increases very rapidly, indicating not only are the latex particles farther apart, but that there is probably a solvation effect. Dilution is critical and should be done very carefully. Two latices that had a difference of 270 seconds at 51.5 per cent total solids differed by 480 seconds at 45 per cent total solids. The lower the total solids content of the sample, the greater the sensitivity of the test; however, this advantage is offset by longer running time. The present recommended dilution of 51.5 per cent total solids appears to be a satisfactory compromise. Extrapolation of the curves in Figure 12 to zero stability time indicates that the total solids would be 69 per cent—the approximate limit of concentrating latex.

Temperature.—The mechanical stability time of a given latex varies inversely with the temperature, and the rate increases rapidly as the temperature of the latex is lowered below room temperature (Figure 13). The stability of a

poor quality latex can be increased from 400 seconds at room temperature to 1800 seconds by cooling to 10° C. This increase is very significant in the storage, aging, and compounding of latex. Heating latex from 25° to 60° C causes a decrease in mechanical stability time, but the rate of change decreases rapidly as the temperature approaches 60° C and the mechanical stability is

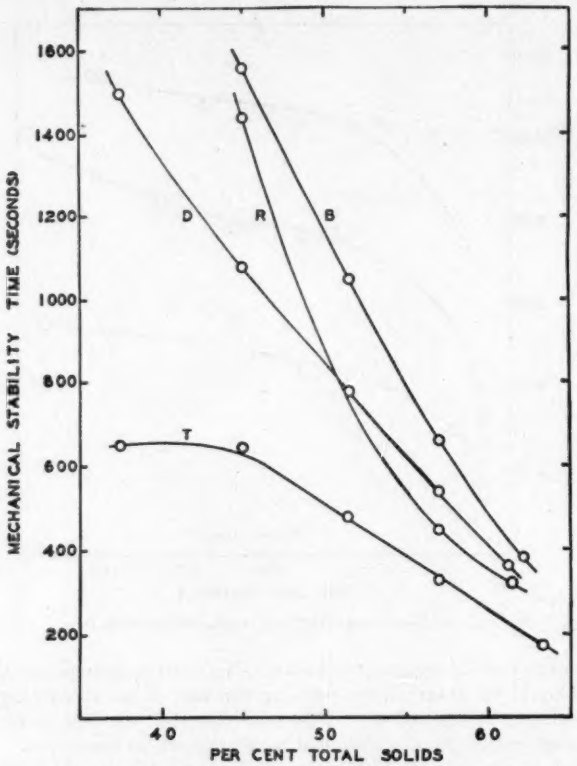


FIG. 12.—Effect of dilution of sample on mechanical stability time.

always low. This is really a combination of two stability tests—heat and mechanical. Therefore temperature is very critical, and close control should be maintained while the test is being run.

MECHANISM OF MECHANICAL STABILITY TEST

High-speed stirring appears to agglomerate or cause the single latex particles to gather into minute clumps or flocs. Van Dalfsen[9] called this microflocculation. If the mechanical force applied is sufficient to overcome the repulsion of like charges on the latex particles (this corresponds to the shear at minimum peripheral speed of the agitator), then the agglomeration takes place at a rate which depends on the probability of particles touching where there is no coating. If the mechanical shear is constant, the time required to reach a certain

degree of agglomeration or coagulation depends on the colloidal characteristics of the latex being tested. In turn the colloidal stability of natural latex depends on the interfacial film[10] between the latex particles and the serum in which they are suspended. This coating is made up of lipides[11], soaps, and proteins, which possess an electric charge[12] and a certain degree of hydration. If one of these

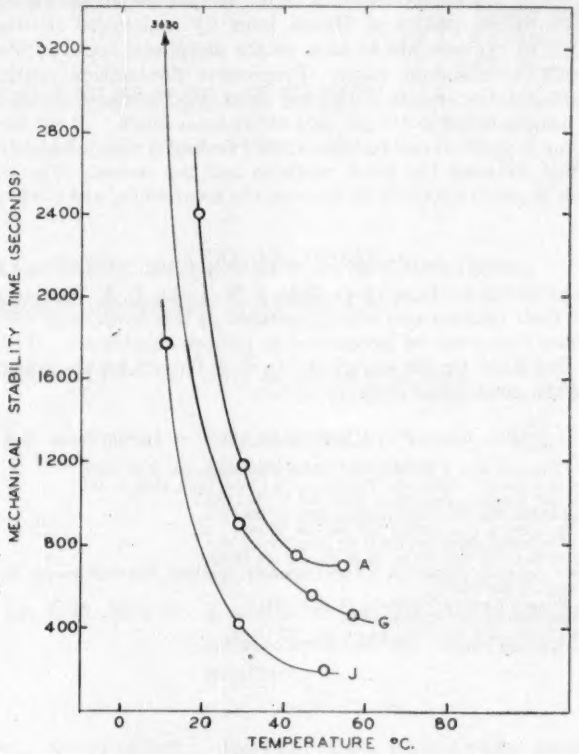


FIG. 13.—Mechanical stability time in relation to temperature of latex sample.

factors is reduced, the stability of the latex is reduced; if one or more of these factors is increased, either by natural reactions in the ammoniated latex during aging[9] or by the addition of proteins, soaps, lipides, or water, the stability of the latex is increased.

The test described is entirely mechanical; the shear or rub takes place at the outer edge of the agitator. This shear is directly proportional to the peripheral speed of the agitator. The process of agglomeration or microflocculation of single latex particles starts as soon as the test is started and proceeds as a result of continual mechanical agitation until the flocs become large enough to be visible without magnification. If stirring is continued, a single large ball of coagulum is produced, which occludes liquid latex. The "end point" is merely an arbitrary stopping point in this progression from billions of single latex particles to one big ball of coagulum. This has been arbitrarily defined as the point

where 0.5 to 1.0 per cent of the total solids has been coagulated to a size large enough to be retained by cheese cloth (Figure 3). Experience has shown that this end point is reproducible with an accuracy of 3 per cent or better.

SUMMARY

The mechanical stability test is a rapid, simple method of estimating the colloidal stability or quality of Hevea latex by high-speed stirring. Latex particles start to agglomerate as soon as the peripheral speed of the agitator reaches a certain minimum value. Progressive flocculation continues until mechanical coagulation occurs. The end point is defined as the time in seconds required to coagulate 0.5 to 1.0 per cent of the total solids. If the shear is constant, the time is proportional to the colloidal stability, which depends upon the interfacial film between the latex particles and the serum. The mechanical stability time depends critically on the size, the total solids, and the temperature of sample.

ACKNOWLEDGMENT

The writer wishes to thank O. D. Cole, J. W. Liska, L. A. Wohler, and E. M. Glymph for their interest and encouragement in this work, and the Firestone Tire & Rubber Company for permission to publish this report. The author is indebted to Joe Koch for the design and to F. S. Grover for the fabrication and assembly of the mechanical stability tester.

REFERENCES

[1] Morris, V. N., Firestone Tire & Rubber Co., private communication, Feb. 1950.
[2] Noble, "Latex in Industry," Palmerton Publishing Co., New York, 1936, p. 181.
[3] Jordan, Brass, and Roe, *Ind. Eng. Chem. Anal. Ed.* 9, 182 (1937).
[4] Murphy, *Proc. Rubber Technol. Conf. London*, 1938, p. 159.
[5] Davey and Coker, *Trans. Inst. Rubber Ind.* 13, 368 (1938).
[6] Martin, *Rev. gén. caoutchouc* 18, 90 (1941).
[7] Novotny and Jordan, *Ind. Eng. Chem. Anal. Ed.* 13, 189 (1941).
[8] Crude Rubber Committee, Division of Rubber Chemistry, American Chemical Society, RUBBER CHEM. & TECHNOL. 14, 290 (1941).
[9] Van Dalfsen, RUBBER CHEM. & TECHNOL. 14, 315 (1941).
[10] Cockbain, *Rubber Age* (N. Y.) 62, 649 (1948).
[11] Homans, Van Dalfsen, and Van Gils, *Nature* 161, 177 (1948).
[12] Seifriz, *Science* 102, 378 (1945).

for ***BUTYL–NATURAL***

or GR-S RUBBERS

specify

NAUGATUCK TUEX

(TETRAMETHYL THIURAM DISULFIDE)

Available as powder or as dustless, fast-dispersing NAUGETS.®

- **in butyl –** Basic acceleration for tubes
- **in natural –** Primary accelerator without sulfur for high heat resistance

  Secondary accelerator with Thiazoles for fast cures in many sundry products
- **in GR-S –** A primary or secondary in general purpose compounding. Fast—but not persistent.

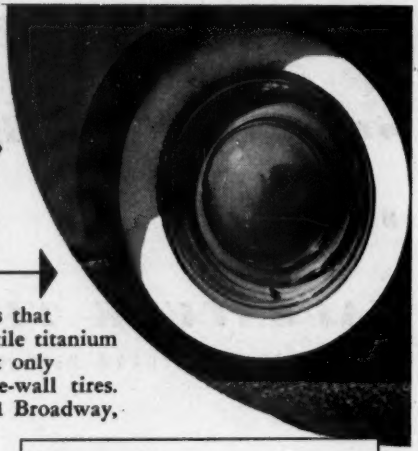
PROCESS – ACCELERATE – PROTECT with NAUGATUCK CHEMICALS

Naugatuck Chemical
Division of United States Rubber Company
NAUGATUCK, CONNECTICUT
In Canada: NAUGATUCK CHEMICALS DIVISION
Dominion Rubber Company Limited, Elmira, Ontario

® *Reg. U.S. Trademark*

reduces checking and chalking

TITANOX-RA-NC



▶Recent experimental work indicates that TITANOX-RA-NC—a "non-chalking" rutile titanium dioxide—is effective for reducing not only chalking but also checking in white-wall tires.

Titanium Pigment Corporation, 111 Broadway, New York 6, N.Y.; 104 South Michigan Avenue, Chicago 3, Ill.; 2600 South Eastern Avenue, Los Angeles 22, Calif. Branches in all other principal cities.

TITANOX
the brightest name in pigments

8056 **TITANIUM PIGMENT CORPORATION**
Subsidiary of NATIONAL LEAD COMPANY

CARBON BLACKS

Wyex (EPC) . . . . . Easy Processing Channel Black
Arrow TX (MPC) . Medium Processing Channel Black
Essex (SRF) . . . . . Semi-Reinforcing Furnace Black
Modulex (HMF) . . . . . High Modulus Furnace Black
Aromex (HAF) . . . . . High Abrasion Furnace Black

CLAYS

Suprex Clay . . . High Reinforcement
Paragon Clay . . . . Easy Processing
Hi-White R . . . . . White Color
Hydratex R . . . . Water Fractionated
RX-43 . . . . Water Fractionated (Super)

RUBBER CHEMICALS

Turgum S, Natac, Butac . . . . Resin-Acid Softeners
Aktone . . . . . Accelerator Activator

HUBER **J. M. HUBER CORPORATION**
342 Madison Ave. New York 17, New York

"Misfit"

formulations may be hiking your production cost

*There's one formulation—and only one—that will keep your manufacturing or processing costs at a minimum. Let UBS "Creative Chemistry" lower your costs and increase production efficiency by recommending formulations tailored to your specific requirements.

Our technical staff will be glad to consider your problems without obligation.

Serving industry with "creative chemistry"

Industrial Latex Adhesives
Rubber Solvent Cements
Synthetic Solvent Cements
Backing Compounds
Combining and Laminating Cements
Coating Compounds
Latex Concentrates
Tank Lining Compounds
Polystyrene Dispersions
Latex Extenders, Tackifiers

. . . Technical data sheets for each product available on request. *Write for yours today!*

Address all inquiries to the Union Bay State Chemical Company, 50 Harvard Street, Cambridge 42, Massachusetts.

Serving Industry with Creative Chemistry

ORGANIC CHEMICALS · SYNTHETIC LATEX · SYNTHETIC RUBBER
PLASTICS · INDUSTRIAL ADHESIVES · DISPERSIONS
COATING COMPOUNDS · LAMINATING MATERIALS · COMBINING CEMENTS

UBS
UNION BAY STATE
Chemical Company

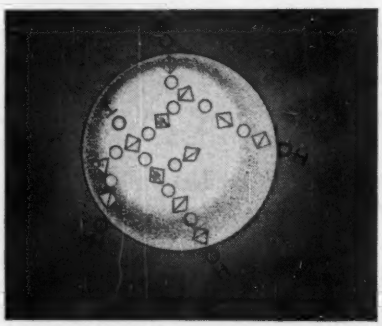
SILICA CHEMISTRY

FOR LATEX PRODUCTS

New chemical approach to latex formulations holds promise for rubber chemists everywhere

More applications for Du Pont "Ludox" colloidal silica in latex goods turn up almost daily. By utilizing the silica chemistry of "Ludox," rubber chemists are now making better latex adhesives, saturants and coatings.

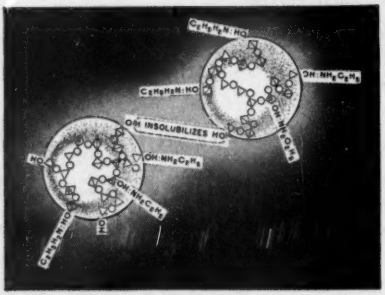
The key to these improvements is the structure of a "Ludox" micelle (*See Fig. 1*). Note surface hydroxyl groups which account for the high chemical reactivity of this 30% colloidal solution of SiO_2. These groups can lead you to entirely new formulations. For example, Figure 2 shows the effect of ethyl amine in bonding with the hydroxyl groups to prevent insolublization of "Ludox" on freezing. This principle is also useful in the stabilization of some latices containing "Ludox."



1

This same mechanism undoubtedly accounts also for the many unusual effects obtained with Du Pont "Ludox." For instance, "Ludox" strengthens—up to three times—latex adhesion to a wide variety of surfaces.

In addition, "Ludox" can double the modulus of neoprene thread, at relatively low loadings. Greatly increased abrasion-resistance, water-resistance,



2

and tensile strength are obtained when "Ludox" is added to neoprene saturants.

These are just a few profitable uses for Du Pont "Ludox" colloidal silica in latex . . . chances are you'll think of others. We will be glad to send you the latest technical bulletin and answer any particular questions you may have. E. I. du Pont de Nemours & Co. (Inc.), Grasselli Chemicals Dept., Wilmington 98, Delaware.

Material for ALL RUBBER and PLASTIC COMPOUNDING

COLORS

FILLERS

SOFTENERS

EXTENDERS

PLASTICIZERS

RESINS . . .
PARA-COUMARON INDENES
HYDRO-CARBON TERPENES
MODIFIED STYRENES
AROMATIC HYDRO-CARBONS

PRECISION Uniformity

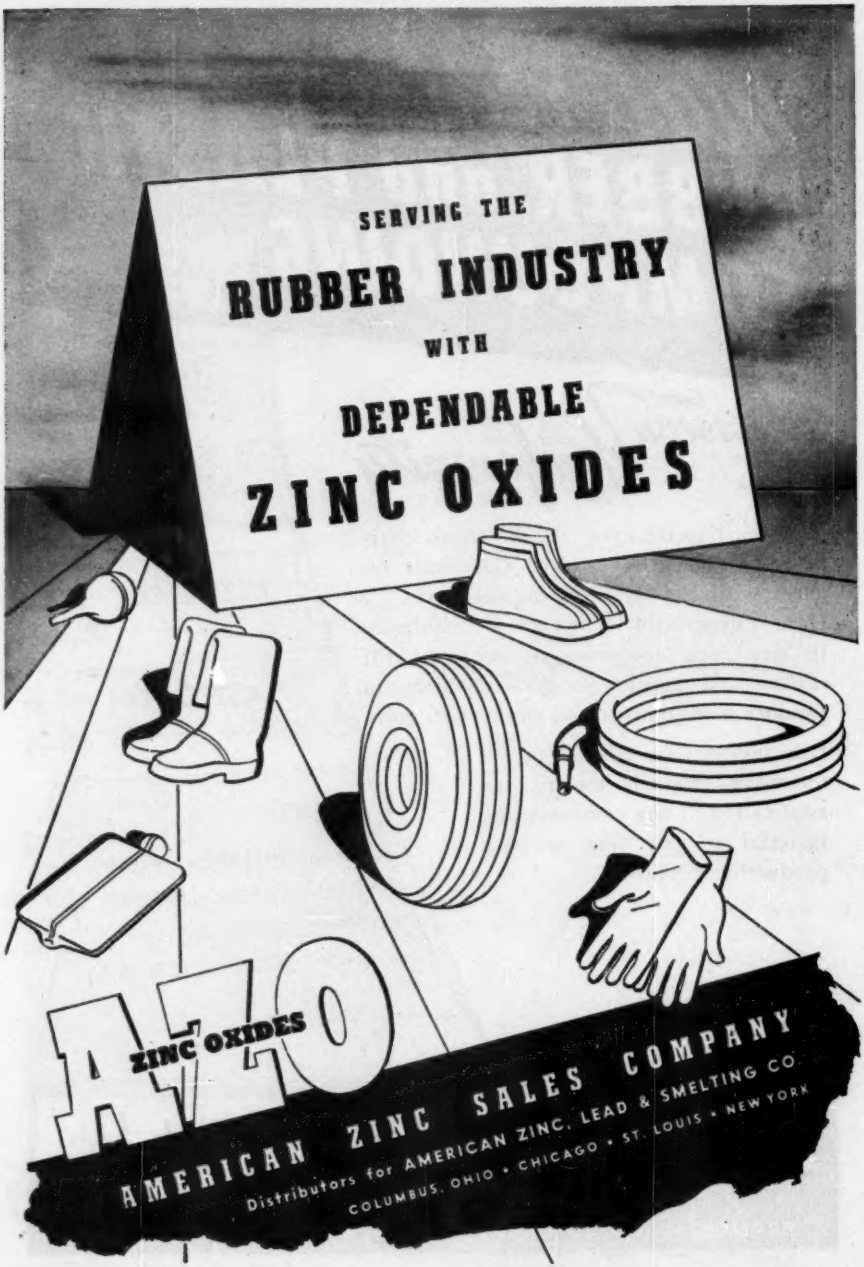
You can depend upon the *Precision* character of Harwick Standard Chemicals regardless of the quantity requirement . . . Here is dependable assurance of uniformity in any type compounding material for rubber and plastics to give *certainty* in product development and production runs.

Our services are offered in co-operative research toward the application of any compounding material in our line to your production problems.

HARWICK STANDARD CHEMICAL CO.

AKRON 5, OHIO

BRANCHES: BOSTON, TRENTON, CHICAGO, LOS ANGELES


SERVING THE
RUBBER INDUSTRY
WITH
DEPENDABLE
ZINC OXIDES
AZO
ZINC OXIDES
AMERICAN ZINC SALES COMPANY
Distributors for AMERICAN ZINC, LEAD & SMELTING CO.
COLUMBUS, OHIO • CHICAGO • ST. LOUIS • NEW YORK

The C.P. Hall Co.
CHEMICAL MANUFACTURERS

ACCELERATORS
PLASTICIZERS
ANTIOXIDANTS

A Complete Line of Approved Compounding Materials

● AKRON, OHIO • LOS ANGELES, CALIF. • CHICAGO, ILL. • NEWARK, N. J.

STAMFORD "FACTICE" VULCANIZED OIL

(Reg. U. S. Pat. Off.)

Our products are engineered to fill every need in natural and synthetic rubber compounding wherever the use of vulcanized oil is indicated.

We point with pride not only to a complete line of solid Brown, White, "Neophax" and "Amberex" grades, but also to our aqueous dispersions and hydrocarbon solutions of "Factice" for use in their appropriate compounds.

Continuing research and development in our laboratory and rigid production control has made us the leader in this field.

The services of our laboratory are at your disposal in solving your compounding problems.

THE STAMFORD RUBBER SUPPLY COMPANY

STAMFORD, CONNECTICUT

Manufacturers of "Factice" Brand Vulcanized Oil
Since 1900

RESEARCH AND DEVELOPMENT

have been keynoted at the St. Joseph Lead Company's Josephtown, Pennsylvania plant since the start of operations in 1931. The fact that this electrothermic zinc smelting installation is unique in the world is, perhaps, the best evidence of the pioneering attitude on which the plant was founded. The several expansions in production rate — which increased the daily processing capacity from 120 tons of zinc concentrate in 1931 to 600 tons per day in 1950 — and the numerous improvements in operational technique during the plant's relatively young life amply justify the abiding philosophy of technological advancement.

The Josephtown plant research group pursues a wide variety of interests of four main types: (1) technical problems arising in regular operations (trouble shooting); (2) improved equipment design and operating methods; (3) development of new equipment, methods and operations; and (4) raising efficiency and lowering costs of existing operations.

An analytical group occupying their own building perform some 75,000 assays annually and are equipped with devices such as the polarograph, pH meter, and colorimeters. A fellowship at the University of Pittsburgh provides access to spectrographic equipment.

The rubber and electronic group are thoroughly equipped for the compounding, curing, and testing of rubber elastomers. In addition to the standard equipment, their facilities include constant temperature and humidity control, a laboratory Banbury mixer, a Mooney viscosimeter and a flexometer of St. Joe design. Electronic testing devices include oscilloscope, vacuum-tube voltmeters, signal generator, and equipment for dielectric constant, power factor, and d-c resistivity measurements. Electron microscope pigment studies have also been provided for.

Paint and varnish testing equipment, indoor and outdoor accelerated aging equipment, and apparatus for evaluating pigment bodying and hiding properties are employed by the paint group.

A ceramic laboratory is maintained for the evaluation of St. Joe Zinc Oxides in various products of the glass, glaze and pottery industries.

Excellent photographic equipment, turbidimeters, colorscope, etc., for work with either pigments or metals are operated by the microscopic and photographic group.

A general physical group is concerned with the quality control of pigments for such properties as particle size, acidity, color, tinting strength and oil absorption, and continuously samples each shift's production for this purpose. Special equipment incident to this type of testing is provided.

Finally, a Pigment Development group is engaged in research on new and improved types of St. Joe Zinc Oxide for the various consuming industries.

ST. JOSEPH LEAD COMPANY · 250 PARK AVENUE · NEW YORK 17

PLANT AND LABORATORY: JOSEPHTOWN, BEAVER COUNTY, PENNSYLVANIA

For Prompt and Complete Coverage of Current Technical and News Developments in the Rubber Industry—

READ

RUBBER AGE

One of the World's Outstanding Rubber Journals

$3.00 a year

★

For Full Information on Rubber Manufacturers and Their Products; Material, Equipment and Services Used by Rubber Manufacturers; Who's Who in the Rubber Industry—

READ

Rubber RED BOOK

Directory of the Rubber Industry

Latest Issue—
1949 Edition

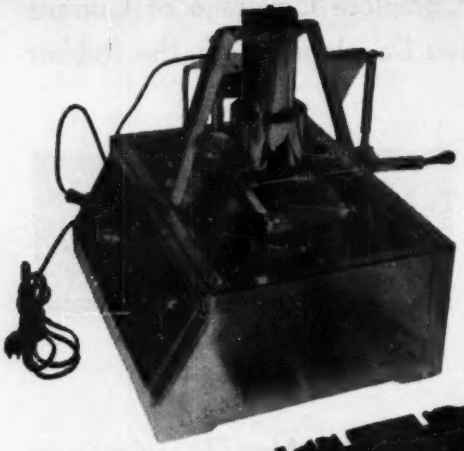
$5.00 a copy

Published By

PALMERTON PUBLISHING COMPANY, Inc.

250 West 57th Street New York 19, N. Y.

TESTED IS TRUSTED



3 Styles Available

1) MODEL E, self contained unit with electric stirrer, control panel, insulated cold tank of stainless steel, as illustrated above. Conforms to ASTM Designation D746.
2) For application to a standard T-50 *Scott Tester (Type A, ASTM Specification D599-40T) apparatus.
3) For installation in existing cold box equipment.

At 3 prices — REQUEST DETAILS

Registered **SCOTT TESTERS** Trademark

SCOTT TESTERS, INC. 102 Blackstone St. Providence, R. I.

Scott Testers — Standard of the World

A *MUST* for every COMPOUNDER OF RUBBER

1947 Second Edition

COMPOUNDING INGREDIENTS FOR RUBBER

The new book presents information on some 2000 separate products as compared to less than 500 in the first edition, with regard to their composition, properties, functions, and suppliers, as used in the present-day compounding of natural and synthetic rubbers. There is also included similar information on natural, synthetic, and reclaimed rubbers as the essential basic raw materials.

Over 600 pages—Cloth Bound
Price $5.00 postpaid in U.S.A.
$6.00 Foreign
(Add 2% Sales Tax for New York City)

INDIA
RUBBER WORLD
386 FOURTH AVENUE NEW YORK 16, N. Y.

RUBBER SUBSTITUTES

(Vulcanized Vegetable Oils)

◆

Manufactured since 1903 by

THE CARTER BELL MFG. CO.

SPRINGFIELD NEW JERSEY

Represented by:

HARWICK STANDARD CHEMICAL CO.

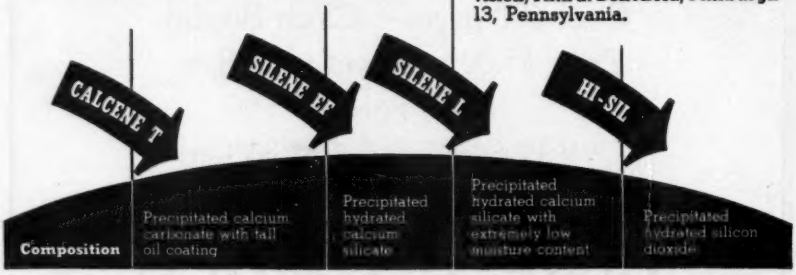
Akron — Boston — Trenton — Chicago — Denver — Los Angeles

It will pay you to get acquainted with this outstanding family of white

COLUMBIA PIGMENTS

Look into these Columbia pigments now. They may provide the answer to your specific rubber compounding problems whether it be cost, compounding, performance or product improvement.

Working samples and technical bulletins on use are available upon request. Pittsburgh Plate Glass Company, Columbia Chemical Division, Fifth at Bellefield, Pittsburgh 13, Pennsylvania.



COLUMBIA CHEMICALS

PAINT · GLASS · CHEMICALS · BRUSHES · PLASTICS

PITTSBURGH PLATE GLASS COMPANY

WHITETEX

A new white and bright pigment for rubber, synthetic rubber or plastics, especially vinyls.

BUCA

A proved pigment for compounding ALL types of natural and synthetic rubber.

CATALPO

For compounding rubber and synthetic rubber.

No. 33 CLAY

For wire and vinyl compounding.

●

For full details, write our Technical Service Dept.

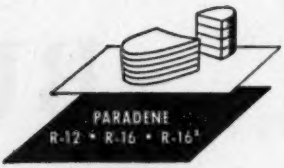
SOUTHERN CLAYS, INC.

(Formerly P. W. Martin Gordon Clays, Inc.)

33 Rector Street · New York 6, N.Y.

How NEVILLE can serve the Rubber Industry

RUBBER SOLES AND HEELS



Improve Product Quality, Save Production Costs, with NEVILLE RESINS

- The coumarone resins are used in the manufacture of rubber soles and heels to reduce set and leatherize the compounds. They are extender-plasticizers which do not lower hardness, tensile, modulus or tear. The grades used generally are medium high melting points and of light to dark color, depending on the color of the stock.
- The most popular grades, in order of lightest color first, are R-13, R-14, R-15, R-16 and R-16A, and the low-cost, quite dark Paradene #2. These resins are also used as extender-plasticizers in compounding the new plastic-type soles.

Chemicals for the Rubber Industry

THE NEVILLE COMPANY
PITTSBURGH 25, PA

STOP RISING COSTS

with

Piccolyte

the versatile resin

Costs Less...Offers More!

Piccolyte—a pure hydrocarbon, thermoplastic terpene resin—is low in cost and readily soluble in low-cost naphthas, pentane and hexane. It is pale and stable in color, chemically inert, compatible with many other materials, non-toxic. There are nine melting points.

Piccolyte has the same carbon to hydrogen ratio as plantation rubber, and has excellent tack-producing properties. Ideal for rubber tile and other products where light colors and tints are demanded.

Use Piccolyte to keep your costs down without sacrificing in any way the quality of your products. Piccolyte costs less per pound today than practically all other resins, yet offers the maximum in quality and service.

Write for data booklet, and a free sample of PICCOLYTE. Give intended use, so we can send sample of appropriate grade.

PENNSYLVANIA
INDUSTRIAL CHEMICAL CORP.
CLAIRTON, PA.

Plants at Clairton, Pa. and Chester, Pa.
Distributed by Harwick Standard Chemical Co., Akron 5, Ohio

ANTIMONY SULPHIDE

Regular Grades *for* Attractive Color

Also

A special grade for obtaining colored stocks having high abrasion resistance

RARE METAL PRODUCTS CO. **ATGLEN, PENNA.**

ADVERTISE *in*

RUBBER CHEMISTRY AND TECHNOLOGY

KEEP YOUR NAME AND YOUR PRODUCTS CONSTANTLY BEFORE THE RUBBER TECHNOLOGIST

Advertising rates and information about available locations may be obtained from E. H. Krismann, Advertising Manager, Rubber Chemistry and Technology, care of E. I. du Pont de Nemours & Company, 40 East Buchtel Ave. at S. High St., Akron 8, Ohio.

THE VANDERBILT MODEL LABORATORY

NORWALK, CONNECTICUT

Here we learn how our materials can be used by our customers to their best advantage. We invite and appreciate your cooperation.

Please feel free to visit our laboratory, to discuss your problems with us and to use our facilities to work them out if you care to do so.

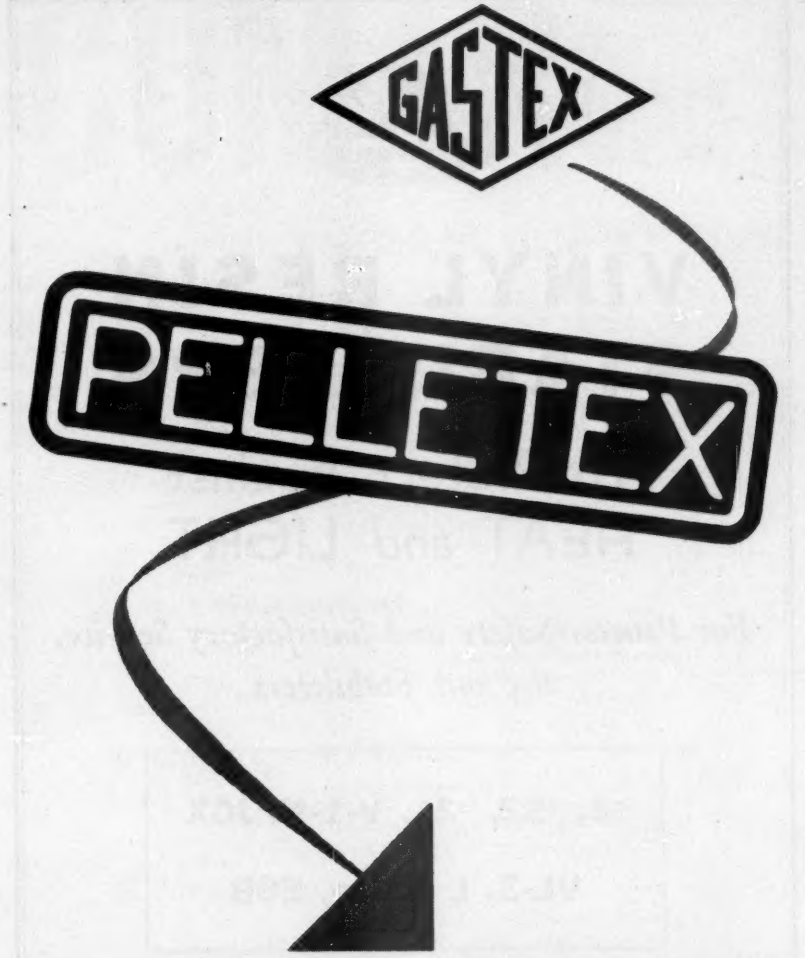
R. T. VANDERBILT CO., Inc.

230 Park Avenue, New York City

RUBBER CHEMISTRY AND TECHNOLOGY IS SUPPORTED BY ADVERTISING FROM THESE LEADING SUPPLIERS

INDEX TO ADVERTISERS

	Page
Advance Solvents & Chemical Corp. (Opposite Inside Back Cover)	34
American Cyanamid Company, Calco Chemical Division	10
American Zinc Sales Company	20
Barrett Div., The, Allied Chemical & Dye Corp. Inside Back Cover	
Binney & Smith Company (Opposite Table of Contents)	14
Cabot, Godfrey L., Inc.	9
Carter Bell Manufacturing Company, The	26
Du Pont Grasselli Chemicals Department	18
Du Pont Rubber Chemicals Division	11
General Atlas Carbon Company	33
Goodrich, B. F., Chemical Company (Hycar)	6
Goodyear Tire & Rubber Company, The	5
Hall, C. P. Company, The	21
Harwick Standard Chemical Company	19
Huber, J. M., Corporation	16
India Rubber World	25
Monsanto Chemical Company	8
Naugatuck Chemical Division (U. S. Rubber Company)	15
Neville Company, The	28
New Jersey Zinc Company, The Outside Back Cover	
Pennsylvania Industrial Chemical Corporation	29
Phillips Chemical Company Opposite Inside Front Cover	1
Pittsburgh Plate Glass Company, Columbia Chemical Div.	26
Rare Metal Products Company	30
Richardson, Sid Carbon Company	7
Rubber Age, The	23
St. Joseph Lead Company	22
Scott Testers, Inc.	24
Sharples Chemicals, Inc.	3
Southern Clays, Inc.	27
Stamford Rubber Supply Company, The	21
Sun Oil Company, Sun Petroleum Products (Opposite Title Page)	12
Thiokol Corporation, The	4
Titanium Pigment Corporation	16
Union Bay State Chemical Company	17
United Carbon Company Inside Front Cover	
Vanderbilt, R. T. Company	31
Witco Chemical Company	2



CARBON BLACKS

THE GENERAL ATLAS CARBON COMPANY
77 Franklin Street, Boston 10, Massachusetts

CABOT

VINYL RESIN STABILIZERS

To Protect Against HEAT *and* LIGHT

For Process Safety and Satisfactory Service, use our Stabilizers

#3, #52, #21, V-1-N, JCX

VL-3, L paste, E6B

CUSTOM MADE SPECIALS TO FIT YOUR NEEDS

Write for Literature

Advance Solvents & Chemical Corp.

245 Fifth Avenue • New York 16, N.Y.

CUMAR* RESIN RH GRADE

IN NATURAL AND SYNTHETIC ELASTOMERS

"CUMAR" Resin, RH Grade, is used to impart many desirable properties to fabricated and laminated items, camelbacks, tire-repair stocks, footwear, printers' rolls, rubber-to-rubber and rubber-to-metal parts, adhesives, cements, and solutions.

1 TO IMPROVE ADHESION

Used in conventional proportions, "CUMAR" Resin, RH grade, does not cause sulfur bloom to occur on raw compounded stocks. It confers tack to the stocks and prevents them from drying out over long storage periods, thus promoting better adhesion.

2 AS A PROCESSING AID

"CUMAR" Resin, RH grade, lowers viscosity, modifies the nerve, and reduces shrinkage; thus contributing to smoother and faster processing, calendering, and extruding properties.

3 FOR EXTENDING THE ELASTOMER

"CUMAR" Resin, RH grade, is unusually effective as an extender. It permits increased loadings with no sacrifice in quality, thus allowing reduced compounding costs.

4 FOR CEMENTS

"CUMAR" Resin, RH grade, accelerates breakdown time of rubber, and improves tack.

5 IN RUBBER-METAL ADHESION APPLICATIONS

"CUMAR" Resin, RH grade, promotes stronger adhesion between rubber and metal. Applied in 2% to 5% solutions in benzol or similar aromatics, the resin forms a tough film on brass-plated or sand-blasted metal surfaces, preventing the formation of rust or scale prior to the application of bonding cement or tie-gum stock.

Barrett

*Reg. U. S. Pat. Off.

THE BARRETT DIVISION
ALLIED CHEMICAL & DYE CORPORATION
40 Rector Street, New York 6, N. Y.

You can formulate *FASTER... BETTER* with

HORSE HEAD® ZINC OXIDES

[redacted]

...Because the Horse Head line comprises the most complete family of Zinc Oxides for rubber:

1. It is the only line having such a wide range of particle sizes, surface conditions and chemical compositions.
2. Its *conventional* types cover the range of American and French Process oxides.
3. Its *exclusive* types include the well-known Kadox and Protox brands.

That means you need not waste time adapting a single Zinc Oxide to each specific compound. Instead, just choose from the Horse Head line the Zinc Oxides that best meet your needs.

[redacted]

...Because you need to compromise less when you choose from the wide variety of Horse Head Zinc Oxides.

...Because the Horse Head brands can improve the properties of your compounds.

Year after year, for nearly a century, more rubber manufacturers have used more tons of Horse Head Zinc Oxides than of any other brands.

THE NEW JERSEY ZINC COMPANY

Founded 1848

160 Front Street, New York 7, N. Y.

RUBBER CHEMISTRY AND TECHNOLOGY

VOL. 24

NOS. 1 – 4

1951

PUB. 184

UNIVERSITY MICROFILMS
ANN ARBOR, MICHIGAN. 1952